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THE PREPARATION AND SPECTROSCOPIC PROPERTIES OF SOME COMPLEXES FORMED BETWEEN VANADIUM (4) OXYDICHLORIDE AND ORGANIC LIGANDS

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The complexes of vanadium (4) oxydichloride with tetrahydrofuran, 1, 2 - dimethoxyethane, pyridine and picolines were prepared having general formulae $\text{VOCl}_2\text{L}'_2$, $\text{VOCl}_2\text{L}'$ and $\text{VOCl}_2\text{L}'\text{L}''$ (here $\text{L}' =$ tetrahydrofuran, and $\text{L}'' =$ 1, 2 - dimethoxyethane, pyridine or picoline). The infrared spectra of complexes were determined in nujol and hexachlorobutadiene (HCB) mull and assignments of vanadium - oxygen double bond ν (V=O), vanadium - oxygen single bond ν (V-O), vanadium - nitrogen ν (V-N), and vanadium - chlorine ν (V-Cl) stretching vibrations were made. The electronic spectra of complexes were determined in dimethoxyethane and toluene solution. The λ_{max} in electronic spectra of the complexes was shifted to longer wavelength by less polar solvent. This red shift in the λ_{max} was discussed by considering that the dipole moment of the complexes was changed during transition. The possible structural formations of the complexes were proposed.

INTRODUCTION

Recent advances in polymerization catalysis have been made using transition metal complexes to obtain a wide variety of new polymers. The successive insertion of monomer molecules between the carbon atom and the metal atom of the catalyst has been responsible for the production of polymers and copolymers of various stereospecific nature. This stereospecificity of polymers has been strongly influenced by the exact nature of the coordination catalyst used.

Complexes of transition metals with a wide variety of ligands have been reported in the literature [1, 2]. Of particular interest are the complexes of vanadium (4) oxydichloride with various electron donating ligands. Vanadium (4) oxydichloride complexes with monodentate ligands other than water have been first reported by Funk and his co-workers [3, 4]. In fact vanadium (4) oxydichloride complexes have been prepared adopting different procedures. Feltz [5] prepared the complexes of VOCl_2 with dioxane and acetonitrile having a general formula VOCl_2L_2 by the partial hydrolysis of VCl_4 in the ligand solutions. Kern [6] and Saito [7] have reported the preparation of VOCl_2 ($\text{C}_4\text{H}_8\text{O}$)₂ by the air oxidation of

VCl_3 ($\text{C}_4\text{H}_8\text{O}$)₃ in the presence of moisture. Baker *et al.* [8] reported the preparation of VOCl_2 complexes by the reduction of vanadium (5) oxytrichloride with mono-, di-, or trimethylamine and a range of thioethers.

An extensive infrared study on VOCl_2 complexes has been undertaken by many researchers [5, 6, 8-13] but even then the far infrared region ($650-200\text{cm}^{-1}$) has yet to be explored. They all reported that the stretching frequencies of vanadium - oxygen double bond, ν (V=O) should be found between 900 and 1100cm^{-1} depending on its environment. The persistent behaviour of the ν (V=O) stretching frequencies in oxovanadium (4) species makes it possible to study the bonding structure of complexes of this d electron system.

The electronic spectra of several oxovanadium (4) complexes [12] have been investigated at room temperature in the spectral region of 1200 to 350 nm. In general, three low intensity absorption bands (ligand field bands) have been observed between 909 to 625 nm, 690 to 526 nm and 476 to 333 nm, respectively. The last band usually overlaps a high intensity charge transfer band and, therefore, appears as a shoulder rather than a distinct absorption peak. The electronic transition of the oxovanadium (4) species depends on their environment. The published data [12] on the electronic spectra of oxovanadium (4) complexes is still limited to establish the effects of solvent on these species.

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In this author's previous paper [14, 15] have been reported the reduction of vanadium (5) oxytrichloride by sulphur to vanadium (4) oxydichloride and henceforth the reactions of VOCl_2 with various organic ligands. The complexes of VOCl_2 with tetrahydrofuran, dimethoxyethane, pyridine and picolines having general formulae $\text{VOCl}_2\text{L}'_2$, $\text{VOCl}_2\text{L}''$ and $\text{VOCl}_2\text{L}'\text{L}''$ are now presented. Infrared and electronic spectra of the complexes are discussed in detail and the structural formations are predicted.

MATERIALS AND METHODS

Vanadium oxytrichloride (K. Light & Co. Ltd.) was purified by fractional distillation under reduced pressure in an anhydrous atmosphere.

Sulphur flowers (Fluorochem Ltd.) were dried at 60° for 48 hr. and then flushed with dry nitrogen for one hr. prior to use.

Tetrahydrofuran, 1, 2 - dimethoxyethane, hexane, toluene, pyridine and picolines (BDH Laboratory Reagents) were purified as described in a previous paper [15].

1. $\text{VOCl}_2(\text{C}_4\text{H}_{10}\text{O}_2)$: This complex was prepared by the reaction of VOCl_2 and 1, 2 - dimethoxyethane. Vanadium (4) oxydichloride used in this experiment was prepared from vanadium (5) oxytrichloride by the reduction of sulphur as described in the previous paper [15]. A mixture of 5 g. VOCl_2 and 250 ml of pure 1,2 dimethoxyethane (DME) was refluxed in a three-necked R.B. flask under the atmosphere of pure nitrogen for 5 hr. The reaction mixture was then filtered while hot and the residual green material was thoroughly washed with pure DME. It was then dried under high vacuum condition ($\sim 10^{-5}$ torr). The $\text{VOCl}_2(\text{C}_4\text{H}_{10}\text{O}_2)$ complex thus prepared was stored in an air-tight flask in a dry box, prior to use in further tests.

2. $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\text{C}_4\text{H}_{10}\text{O}_2)$: This complex was prepared by the reaction of $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})_2$ and DME adopting two slightly different procedures. $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})_2$ used in this experiment was prepared by the reaction of VOCl_2 with tetrahydrofuran as described in the previous paper [15]. 1. A mixture of 9.9 g. of $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})_2$, 6.3 g. of DME and 100 ml of pure tetrahydrofuran was charged in a three-necked R.B. flask and stirred for 1 hr. in an atmosphere of pure nitrogen. The reaction mixture was then allowed to stand for 16 hr. During this time the precipitate of $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\text{C}_4\text{H}_{10}\text{O}_2)$ appeared and it was filtered and dried under high vacuum conditions. 2. In the second experiment DME was used as a ligand as well as a solvent. Thus $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})_2$, 5 g., and 100 ml of DME was stirred in a three-necked R.B. flask in an atmosphere of nitrogen. The reaction was observed by the gradual change of colour from green, $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})_2$ to purple $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\text{C}_4\text{H}_{10}\text{O}_2)$ which reached completion within a few minutes. The excess DME was filtered off and the residual material was dried under high vacuum conditions.

$\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\text{C}_5\text{H}_5\text{N})$: This complex was prepared by the reaction of $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})_2$ and pyridine in tetrahydrofuran. A mixture of $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})_2$, 5.64 g, and pyridine 1.58 g, 1:1 molar ratio in 50 ml of pure tetrahydrofuran was stirred for 3 hr. under the atmosphere of nitrogen. The reaction mixture was then allowed to stand for three days. During this time solid $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\text{C}_5\text{H}_5\text{N})$ appeared, which was recovered by filtration. The complex thus prepared was dried under high vacuum conditions and then stored in an air-tight flask in a dry box before further use.

$\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\alpha - \text{C}_6\text{H}_7\text{N})$, $\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})$

Table 1. Yield and Analytical Data for the Complexes of Vanadium (4) Oxydichloride.

Compound*	Yield %	C%		H%		N%		Cl%	
		Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.
$\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})_2$	53	34.1	33.9	5.7	5.7	—	—	25.2	25.2
$\text{VOCl}_2(\text{C}_4\text{H}_{10}\text{O}_2)$	85	21.0	19.6	4.3	4.0	—	—	31.2	31.5
$\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\text{C}_4\text{H}_{10}\text{O}_2)$	95	32.0	32.0	6.0	5.9	—	—	23.7	23.9
$\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\text{C}_5\text{H}_5\text{N})$	90	37.4	37.4	4.5	4.6	4.8	4.8	24.6	25.0
$\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\alpha - \text{C}_6\text{H}_7\text{N})$	93	39.6	39.6	5.0	5.4	4.6	4.7	23.4	23.7
$\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\beta - \text{C}_6\text{H}_7\text{N})$	94	39.6	39.5	5.0	5.3	4.6	4.9	23.4	23.4
$\text{VOCl}_2(\text{C}_4\text{H}_8\text{O})(\gamma - \text{C}_6\text{H}_7\text{N})$	92	39.6	39.8	5.0	4.8	4.6	5.4	23.4	23.9

* Here $\text{C}_4\text{H}_8\text{O}$ is tetrahydrofuran, $\text{C}_4\text{H}_{10}\text{O}_2$ is 1, 2-dimethoxyethane, $\text{C}_5\text{H}_5\text{N}$ is pyridine and $\alpha -$, $\beta -$, and $\gamma - \text{C}_6\text{H}_7\text{N}$ are picolines.

(β - C_6H_7N) and $VOCl_2(C_4H_8O)$ (γ - C_6H_7N) were prepared by the reaction of $VOCl_2(C_4H_8O)_2$ with the respective picoline in tetrahydrofuran using the same molar ratio of the reactants and the procedure as described for the preparation of $VOCl_2(C_4H_8O)(C_5H_5N)$.

Elemental analyses were carried out on all the complexes for carbon, hydrogen, nitrogen and chlorine. The results are summarised in Table 1.

Infrared spectra of all the complexes were recorded in nujol and HCB mulls using a Perkin Elmer Model 621 Spectrophotometer. The mull was always prepared in a dry box to avoid contamination of the complex with atmospheric moisture. The values of diagnostic infrared absorption frequencies (cm^{-1}) and band assignments of the complexes are given in Table 2. The frequencies given should be considered accurate to $\pm 2cm^{-1}$.

The electronic spectra of the complexes were measured

in a closed absorption cell apparatus, consisting of a 10 mm path length quartz cell. The samples were weighed in an air tight ampoule and the solutions were then prepared in a dry box using pure toluene and DME. The spectra were recorded using Unicam SP 700 Spectrophotometer. All the results are summarised in Table 3.

DISCUSSION

Vanadium (4) oxydichloride complexes having a general formula $VOCl_2 L L$ were prepared by the reaction of $VOCl_2(C_4H_8O)_2$ and pyridine or picolines in tetrahydrofuran. A similar procedure has been adopted for the preparation of $VOCl_2$ complexes with pyridine and picolines having general formulae, $VOCl_2 L_2$ and $VOCl_2 L_3$ in the previous paper [15] but here 1:1 molar ratio of $VOCl_2(C_4H_8O)_2$ to ligand was used to replace only one molecule

Table 2. Infrared Absorption Frequencies (cm^{-1}) and Bond Assignments for the Complexes of Vanadium (4) Oxydichloride.

Compound	$\nu(V=O)$.	$\nu(V-N)$.	$\nu(V-Cl)$.	$\nu(V-O)$ or $\nu(V-N)$ or $\nu(V-Cl)$.
$VOCl_2(C_4H_8O)_2$	902(S)	—	376(S) 327(S)	282(m) 238(m)
$VOCl_2(C_4H_{10}O_2)$	900(S)	—	366(S) 350(Sh.)	440(m) 322(m) 298(m)
$VOCl_2(C_4H_8O)(C_4H_{10}O_2)$	972(S)	—	390(Sh.) 340(S)	680(m) 552(m) 405(S) 266(m)
$VOCl_2(C_4H_8O)(C_5H_5N)$	985(S)	440(S) 442(S)	362(S) 313(S)	642(S) 280(m) 225(m)
$VOCl_2(C_4H_8O)(\gamma-C_6H_7N)$	1010(S)	444(S)	384(S) 312(S)	648(m) 340(m) 290(Sh.)
$VOCl_2(C_4H_8O)(\beta-C_6H_7N)$	982(S)	418(S)	377(S) 312(S)	345(S) 276(m)
$VOCl_2(C_4H_8O)(\gamma-C_6H_7N)$	985(S)	552(S) 492(S)	380(S) 310(S)	350(S) 380(m) 366(Sh.)

S = strong, m = medium and Sh. = shoulder.

Table 3. Colour and Electronic Absorption Spectral Values of the Complexes of Vanadium (IV) Oxydichloride.

Compound	Colour	Solvent	λ max. (nm)	$\epsilon \lambda$ max.	λ max. (nm)	$\epsilon \lambda$ max.	λ max. (nm)
VOCl ₂ (C ₄ H ₈ O) ₂	Green	DME	683	17.3	820	13.6	351(Sh.)
		Toluene	725	—	795	—	480
VOCl ₂ (C ₄ H ₁₀ O ₂)	Green	DME	676	34.1	775	30.8	705(Sh.)
		Toluene	—	—	—	—	—
VOCl ₂ (C ₄ H ₈ O)(C ₄ H ₁₀ O ₂)	Purple	DME	676	21.7	814	18.1	345(Sh.)
		Toluene	730	—	795	—	—
VOCl ₂ (C ₄ H ₈ O)(C ₅ H ₅ N)	Green	DME	714	23.7	820	25.3	702(Sh.)
		Toluene	733	—	820	—	—
VOCl ₂ (C ₄ H ₈ O)(γ -C ₆ H ₇ N)	Green	DME	683	40.6	863	42.2	377(Sh.)
		Toluene	782	—	—	—	—
VOCl ₂ (C ₄ H ₈ O)(β -C ₆ H ₇ N)	Green	DME	686	31.7	827	28.7	—
		Toluene	736	—	833	—	—
VOCl ₂ (C ₄ H ₈ O)(γ -C ₆ H ₇ N)	Blue	DME	718	26.8	820	29.2	645(Sh.)
		Toluene	725	—	820	—	—

Sh = shoulder

of tetrahydrofuran by the stronger field ligand pyridine or picoline. It seems very unlikely from the results that the end product of the reaction between VOCl₂ (C₄H₈O)₂ and pyridine/picoline contains a mixture of VOCl₂ (C₅H₅N)/VOCl₂ (C₆H₇N)₂ and unreacted VOCl₂ (C₄H₈O)₂ because the VOCl₂ (C₄H₈O)₂ complex is very soluble in tetrahydrofuran and can easily be separated by filtration while VOCl₂ (C₄H₈O)(C₅H₅N) and VOCl₂ (C₄H₈O)(C₆H₇N) are insoluble and can only be purified by washing with tetrahydrofuran.

It was found in the preparation of the VOCl₂ (C₄H₈O)(C₄H₁₀O₂) complex that one molecule of tetrahydrofuran from VOCl₂ (C₄H₈O)₂ can be replaced by one molecule of DME and furthermore DME behaves as a monodentate rather than a bidentate ligand. The slightly higher value of dielectric constant of tetrahydrofuran (7.39) than DME (7.2) at 25° does not explain these results. However, it is known [16] that DME due to its probable bidentate behaviour acts as a much more powerful coordinating agent than tetrahydrofuran. In fact the formation of VOCl₂ (C₄H₁₀O₂) complex explain the bidentate ligation of DME.

In the previous paper [15] this author has described the preparation of VOCl₂ (C₅H₅N)₄ by the reaction of VOCl₂ with pyridine under very mild experimental condi-

tions but to prepare a VOCl₂ complex with four molecules of tetrahydrofuran or DME was not possible even under the relative harsh experimental conditions (reflux temperature). These results can be explained by considering that the coordination of a Lewis acid (VOCl₂) with a ligand depends mainly on the ligational strength of the ligand, and in other words, the electron-pair donating ability of the Lewis base. Infrared absorption frequencies (cm⁻¹) for (V = 0) are listed in Table 2 for VOCl₂ complexes. The vanadium - oxygen multiple bond, $\nu(V = 0)$ stretching frequencies are the most significant in the infrared spectral studies of the complexes. The strong absorption bands appearing in the frequency region of 900 to 1010cm⁻¹ can be considered the diagnostic bands showing the presence of vanadium - oxygen multiple bond. The variation in (V = 0) stretching frequency depends on its environment. The stretching frequencies of vanadium - oxygen multiple bond $\nu(V = 0)$ observed for the VOCl₂ complexes with oxygen, and with both oxygen - nitrogen containing ligands suggest that the shift to higher frequencies for the latter set of complexes is due to the transfer of increasing amounts of charge onto the vanadium by ligands of increasing donor strength. The $\nu(V = 0)$ variation found for VOCl₂ (C₄H₈O)₂ and VOCl₂ (C₄H₈O)(C₄H₁₀O₂) complexes might be explained by considering

the caging effect of the bulky ligand molecule over ($V = 0$) species. This caging effect is also quite significant in picoline complexes where $\nu(V = 0)$ for $VOCl_2(C_4H_8O)$ ($\alpha-C_6H_7N$) is 1010cm^{-1} as compared to 982 and 985cm^{-1} for an equivalent complex of β -, γ -picoline, respectively.

The vanadium - oxygen single bond stretching frequencies, $\nu(V - O)$ are also listed in Table 2 for all the complexes. The investigation of these bands is of considerable importance because it provides information about the nature of metal - oxygen bond. In fact it has been reported by Nakamoto *et al.* [17] and Gamo [18] in their infrared study of inorganic salts with coordinated water that the metal - oxygen bands in the NaCl region were observable only when the water molecules were linked to the metal by fairly covalent bonds and also to the outer ion or the ligand of the neighbouring complex by strong hydrogen bonds. They assigned these bands varying from 880 to 650cm^{-1} . The fact that no explanation has been offered with respect to the frequency spread may be due to insufficient data. The vanadium - oxygen stretching bands are observed at 870 to 845cm^{-1} for $VOCl_2$ complexes with oxygen containing ligands. The vanadium - oxygen stretching frequency spread found for these complexes is very small compared to its reported [19] spread for various complexes of transition metals with coordinated water. There may be several reasons responsible for this frequency spread, e.g. (1) oxidation state of the metal ion, (2) size of the metal ion, (3) environment of the metal ion, and (4) the covalent nature of the metal to oxygen bond. The shift to lower frequencies of $\nu(V - O)$ stretching observed for the complexes having a general formula $VOCl_2 L' L''$ can be related to the ligand L' in the following order: α - picoline $<$ β picoline $<$ γ picoline = pyridine.

The vanadium - nitrogen, $\nu(V - N)$ stretching frequency is of significant importance too, because it provides valuable information about the coordinate bond. The $\nu(V - N)$ should appear in the lower frequency region because of the relatively heavy mass of the coordinate bond. The bond assignments for $\nu(V - N)$ stretching vibrations of the $VOCl_2$ complexes are given in Table 2. The $\nu(V - N)$ stretching frequencies found for these complexes correspond to the values reported in the previous paper [15] for the $VOCl_2$ complexes of respective ligands with a maximum difference of $\pm 2\text{cm}^{-1}$. In accordance with these results it can be suggested that the ($V - N$) stretching frequencies in pyridine and picoline complexes are not apparently dependent upon the environment of the vanadium ion as is the case in metal - aniline complexes [20]. The frequencies designated for ($V - N$) modes are

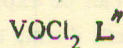
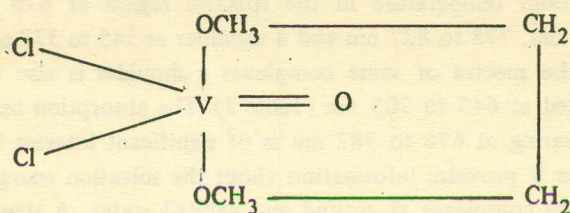
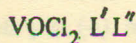
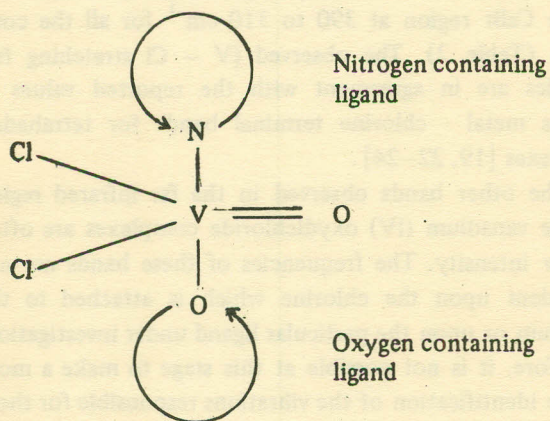
in good agreement with the predictions of Bicelli [21] which were based on an empirical relationship involving the carbon - nitrogen bonds in the pyridine ring.

The fourth series of bands under discussion are the vanadium - chlorine, $\nu(V - Cl)$ stretching modes. The metal - halogen stretching bands can be very useful to determine the structure of a complex by comparing the number of observed bands with that predicted from Group Theory [19]. The ($V - Cl$) stretching frequency bands are observed in the CsBr region at 390 to 310cm^{-1} for all the complexes (Table 2). The observed ($V - Cl$) stretching frequencies are in agreement with the reported values of various metal - chlorine terminal bands for tetrahedral complexes [19, 22-24].

The other bands observed in the far infrared region for the vanadium (IV) oxydichloride complexes are often of low intensity. The frequencies of these bands are not dependent upon the chlorine which is attached to the vanadium or upon the particular ligand under investigation. Therefore, it is not possible at this stage to make a more precise identification of the vibrations responsible for these bands.

In order to establish the effect of solvent on the electronic spectra of vanadium (4) oxydichloride complexes, the spectra are studied in DME and toluene. In general, two low intensity absorption bands are observed at room temperature in the spectral region at 676 to 782nm , 775 to 827nm and a shoulder at 345 to 377nm . In the spectra of some complexes a shoulder is also appeared at 645 to 705nm (Table 3). The absorption band appearing at 676 to 782nm is of significant interest because it provides information about the solvation energies of the complexes at ground and excited states. A significant red shift observed in this spectral region for all the complexes in toluene can be explained by considering the change in dipole moment during the transition. It is known [25] that a molecule that is polar in its ground state will have in its excited state an altered dipole moment which may be greater or less than the ground state moment. The decrease for the vanadium (4) oxydichloride complexes with respect to dipole at the excited state results in the decrease of solvation energy for this state relative to the ground state through the dipole polarisation forces. Consequently, a blue shift in the solution spectra of complexes will appear depending on the refractive index of the solvent and on the change in the dipole moment of the complex. This shift should overlap the polarisation red shift and the resultant shift may be either red or blue depending on the relative magnitudes of two effects. On the other hand, if the dipole moment of the complexes increases during the

transition, the solvation energy of the excited state will increase relative to the ground state and hence the solution spectra of the complexes will shift to the red by an amount depending on the refractive index of solvent. The spectroscopic investigations in conjunction with the elemental analyses of the complexes have the stoichiometry VOCl_2L_2 are in agreement with the reported structural formation of $\text{VOCl}_2(\text{NMe}_3)_2$ [8, 26].



The structural formation of $\text{VOCl}_2(\text{C}_4\text{H}_{10}\text{O}_2)$ complex where DME behaves as a bidentate should be a twisted form of structure as described for $\text{VOCl}_2 \text{L}' \text{L}''$.

REFERENCES

- J.C. Bailor, *Chemistry of Coordination Compounds* (Reinhold, New York, 1956).
- F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions* (Academic Press, New York, 1949).
- H. Funk and W. Weiss, *Z. Anorg. Allgem. Chem.*, **296**, 36 (1958).
- H. Funk, G. Mohaupt and A. Paul, *Z. Anorg. Allgem. Chem.*, **302**, 199 (1959).
- A. Feltz, *Z. Anorg. Allgem. Chem.*, **354**, 225 (1967).
- R.J. Kern, *J. Inorg. Nucl. Chem.*, **24**, 1105 (1962).
- M. Saito, Pat. No. 2939/68, Japan (1968).
- K.L. Baker, D.A. Edwards, G.W.A. Fowles and R.G. Williams, *J. Inorg. Nucl. Chem.*, **29**, 1881 (1967).
- J. Selbin and L.H. Holmes Jr., *ibid.*, **24**, 1111 (1962).
- J. Selbin, L.H. Homes Jr., and S.P. McGlynn, *Chem. Ind. (London)*, 746, (1961).
- J. Selbin, L.H. Holmes Jr., and S.P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359, (1963).
- J. Selbin, *Chem. Rev.*, **65**, 153 (1965).
- C.G. Barraclough, J. Lewis and R.S. Nyholm, *J. Chem. Soc.*, 3552, (1959).
- A.K. Datta and M.A. Hamid, *Z. Anorg. Allgem. Chem.* **407**, 75 (1974).
- M.A. Hamid, *Pakistan, J. Sci. Ind. Res.*, **20**, 330 (1977).
- T.E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).
- J. Fujita, K. Nakamoto and M. Kobayashi, *Ibid.*, **78**, 3963 (1956).
- I. Gamo, *Bull. Chem. Soc. (Japan)*, **34**, 760, 765, 1430, 1433 (1961).
- K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed., Wiley, New York (1963).
- I.S. Ahuja, D.H. Brown, R.H. Nuttall and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **27** (7), 1625 (1965).
- L. Peraldo-Bicelli, *Ann. Chim. (Rome)*, **48**, 749 (1958).
- R.J.H. Clark and C.S. Williams, *Chem. Ind. (London)*, 1317 (1964).
- J.R. Allan, D.H. Brown, R.H. Nuttall and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1305 (1965).
- R.J.H. Clark and C.S. Williams, *Inorg. Chem.*, **4**, 350 (1965).
- N.D. Coggeshall and E.M. Lang, *J. Am. Chem. Soc.*, **70**, 3283 (1948).
- J.E. Drake, J. Vekris and J.S. Wood, *J. Chem. Soc., (A)*, 1000 (1968).