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STUDIES ON COORDINATION COMPOUNDS

Part IV.—Adipyl Dihydrazide Complexes of Copper, Zinc and Cadmium

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Adipyl dihydrazide (ADH) complexes of the type ADH.MX_2 where X = Cl, Br, NO_3 or $\frac{1}{2}SO_4$ and M=Cu, Zn or Cd, ADH$(MX_2)_n$ where $n = 3$ or 4 and X = Cl or $\frac{1}{2}SO_4$ for M = Cu and $n = 2$ and X = Cl or Br for M = Cd and $ADH_3(MX_2)_4$ where M = Cu and X = Cl or Br have been prepared. Unstable compounds of the type (Cu_2AdipatoX_2) where X = Br or NO_3 have also been obtained which indicate the reducing properties of the ligand. This property is suggested to be responsible for stabilizing the bridged polynuclear clusters. The bridged structure gives lower magnetic moments whereas the monochelates of copper have normal values. The stability constant for the former class of compounds is higher than for the latter. The IR spectra have been discussed with respect to the NH_2 rocking frequencies and it is suggested that the amido nitrogen is linked to the copper atom, whereas the amino nitrogen is bonded to the other metals in their respective complexes.

Previous papers[1,2] have described the nickel and cobalt complexes of adipyl dihydrazide (ADH). This ligand has been found to form coordination polymers. From the shift in the C=O absorption to higher and NH_2 frequency to lower wavelengths, it was shown that the metal was bonded through nitrogen. This was also supported by the higher ligand field parameters characteristic of nitrogen bonded complexes. During the preparation of the copper complexes which are being reported here, it has been noted that when the metal salt is refluxed with the ligand, cuprous chloride and adipic acid are two of the main products. Under mild conditions a variety of crystalline products with various metal to ligand ratios are also obtained. The same is also true of the cadmium complexes. The present study is therefore concerned with the preparation of the copper, zinc and cadmium complexes which seem to form bridged complexes. The chelate in the case of the sulphates of these metals are also being reported.

Experimental

The analyses were done by the Schwarzkopf Microanalytical Laboratory, New York, and the Microanalytical Section of these Laboratories. The IR spectra were recorded on Beckman IR10 spectrophotometer. Magnetic susceptibility was measured on a Gouy balance (donated by the CENTO Aid Agency).

Two methods of preparation were followed:

(1) The metallic salt and the ligand were refluxed in less than the requisite stoichiometric amount, and (2) the salt was reacted with an excess of ligand (approximately 2.5 equivalents). A series of products with varying metal–ligand ratio were obtained whose analytical data are listed in Table 1.

When the ligand and cupric chloride were refluxed by method 1 in aqueous medium, it was found that after 30 min crystals of cuprous chloride started depositing. When the solution was evaporated off crystals of adipic acid (Analysis: C, 48.52, H, 6.84; N, 0.0. Calc. for $C_6H_{10}O_4$: C, 49.3; H, 6.84%), were isolated. For copper bromide and nitrate the solids obtained by method 1 gave an analysis corresponding to cupricadipato bromide (III) or nitrate (IV) with the general formula Cu_2(Adipato)X_2. These two are dark green compounds and are paramagnetic so that they are not a mixture of adipic acid and cuprous salts which would be diamagnetic. They do decompose on standing and give a black solid for the bromide and the IR shows the presence of free adipic acid (Table 2). However, when the reaction was carried out by warming the reactants by method 2 and setting aside to cool, amorphous solids were obtained in the case of copper sulphate and chloride. Each of these solids could be formulated as ADH$(CuX_2)_n$ where X = Cl or $\frac{1}{2}SO_4$ and $n = 3$ for the sulphate (II) and 4 for the chloride (I).

When an aqueous solution of the ligand was added to two equivalents of copper chloride, bromide or sulphate and set aside for 24 hr dark green crystals of the complexes having metal–ligand ratio of 4:3 were obtained for the chloride (V) and bromide (VI) and deep blue crystals of the sulphate (VII) with a ratio of 1:1 were obtained.

TABLE 1.—CHARACTERIZATION OF ADH COMPLEXES.

Complexes	Colour	M.P. (°C)	C% Cal.	C% Found	H% Calc.	H% Found	X% Calc.	X% Found
I $[ADH(CuCl_2)_4]8H_2O$	Light blue	160	8.43	9.11	3.51	3.82	6.56	6.19
II $[ADH(CuSO_4)_3]3H_2O$	,,	270	10.21	10.8	2.83	3.78	7.94	7.25
III $[Cu_2Adipato]Br_2$	Green	120	16.66	15.81	2.71	2.4	0.0	0.0
IV $[Cu_2Adipato](NO_3)$	Green	155	18.18	18.82	2.58	3.60	7.07	7.81
V $[(ADH)_3(CuCl_2)_4]8H_2O$	Dark green	110	17.96	17.43	4.82	3.82	23.62	23.92
VI $[(ADH)_3(CuBr_2)_4]4H_2O$	,,	175	14.53	14.18	3.36	3.052	43.00	42.27
VII $[ADH(CuSO_4]2H_2O$	Dark blue	225	19.72	19.63	4.93	5.5	—	—
VIII $[ADH(CdCl_2)_2]$	white	305	13.31	13.56	2.58	2.97	26.26	24.61
IX $[ADH(CdBr_2)]6H_2O$	,,	308	8.71	8.63	2.90	2.48	—	—
X $[ADH\ CdBr_2]$	,,	90	16.14	16.49	3.14	4.04	—	—
XI $[ADHCd(NO_3)_2]2H_2O$	,,	190	16.14	17.00	4.03	3.87	18.83	18.74
XII $[ADHCdSO_4]H_2O$	,,	335	18.02	18.08	4.03	4.17	—	—
XIII $[ADHZnSO_4]2H_2O$	,,	250	19.41	19.6	4.85	5.13	—	—

X = Chlorine or Bromine

TABLE 2.—MAGNETIC SUSCEPTIBILITY OF THE COMPOUNDS.

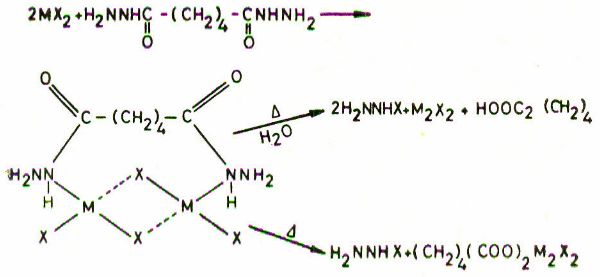
Compounds	Temp °C	$Xg \times 10^{-6}$	$Xm—10^{-6}$	Corrected $Xm \times 10^{-6}$	X/g-atom × 10^{-6}	eff.B.M.
I $[ADH(CuCl_4)_4]8H_2O$	30	5.14	4392	4702.2	1175.6	1.34
II $[ADH(CuSO_4)_3]3H_2O$	30	3.95	2781	2999.07	999.7	1.56
IV $[(Cu_2Adipato)](NO_3)_2$	20	2.82	941.7	1040.14	1040.14	1.57
V $[(ADH)\,!(CuCl_3)]8H_2O$	20	2.09	2741	2958.5	739.6	1.32
VI $[(ADH)_3(CuBr_2)_4]4H_2O$	20	2.15	3217	3703.6	936.4	1.48
VII $[ADHCuSO_4]2H_2O$	20	2.79	1282	1409.6	1409.6	1.82

In a similar manner the 2:1 complexes were obtained for cadmium chloride and bromide (IX) and 1:1 complexes for cadmium bromide(X), nitrate (XI) and sulphate (XII) and for zinc sulphate (XIII).

Results and Discussion

A wide range of complexes with varying stoichiometry is obtained from the metal salts and adipyl dihydrazide. The metal–ligand ratio is in no case less than one. In the previous papers the complexes of nickel and cobalt also did not have the same stoichiometry among themselves.

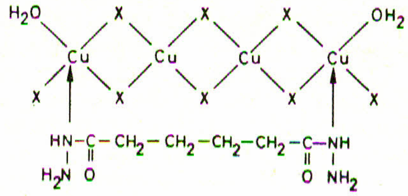
The bonding in the nickel and cobalt complexes was shown to occur through the amino nitrogen. In the case of copper, reduction of cupric chloride to cuprous chloride along with the formation of adipic acid and also the isolation of adipato bromide(III) and nitrate(IV) suggest that the metal is bonded through the amide nitrogen.



Scheme 1

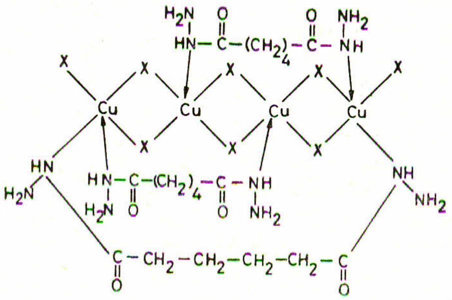
Thus the initial N—N→M bond is cleared by boiling according to Scheme. We have been able to isolate all the products except the hydrazine salt which possibly volatilizes off.

The isolation of complexes of the type $ADH_3(CuX_2)_4$ and $ADH(CuX_2)\,n$ where $n = 3$ for SO_4 and 4 for Cl shows that these are bridged complexes of the type A.



A

The complexes of the type $ADH_3(CuX_2)_4$ for both the chloride and the bromide should then be formulated as



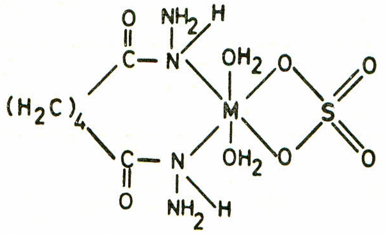
B

which shows that the complexes are octahedral in the former case and are distorted octahedral or tetrahedral in the latter. The 1:1 copper sulphate complex (VII) has a chelate structure with both the amide groups taking part in coordination and again has distorted octahedral structure.

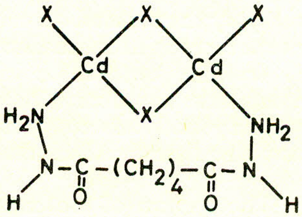
The structure for the two series of copper complexes are supported by their magnetic data. The ADH$_3$(CuX$_2$)$_4$ complexes have $\mu_{\text{eff.}} = 1.32$ and 1.48 B.M. respectively for the chloride and bromide which are similar to ADH(CuX$_2$)$_n$ having a magnetic moment of 1.34 and 1.56 B.M. respectively for the chloride and sulphate. The nitrate (IV) has an intermediate value of 1.57 B.M. while the sulphate has a normal value of 1.82 B.M. The low values of the ADH$_3$(CuX$_2$)$_4$ or ADH(CuX$_2$)$_n$ complexes is similar to those reported for the binuclear bisamine copper formates.[3] The polynuclear bridged halides of copper are well-known. These complexes are obtained under mild conditions which are not disturbing the bridged structure. The polynuclear octahedral configuration of the type B might then be a preferred structure as is true of paramagnetic clusters. This preference for the formation of clusters must be due to the stabilization imparted by the reducing action of the ligand. The formation of cuprous chloride suggests that there is a reduction in the magnitude of the residual positive charge on each copper and a reduction of this type in the electrostatic charge gives stability to the bridged structure which is responsible for the low magnetic moments of the complexes.[3] The stability is also imparted by the Jahn–Teller distortions along the elongated axis.[4]

The complexes of the type ADH(CuX$_2$)$_n$ are most probably of the type A with a distorted octahedral or tetrahedral configuration. But the similarity in magnetic moment suggests that the bridged structure is present here also. It must be noted that a structure of this type owes its stability to the chelate effect of the ligand and it is here that the complexes have been found to be converted to the adipato bromide and nitrate. This shows that just one ligand in the A type complexes is not sufficient to stabilize the bridged structure.

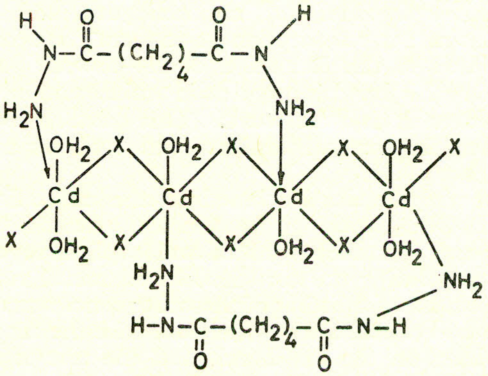
The ADH.CuX$_2$ complexes, of which only the sulphate ADH.CuSO$_4$2H$_2$O has been isolated might be a chelate. This is a crystalline solid, very slightly soluble in water and organic solvents and is not like the nickel or cobalt complexes for which a polymeric structure has been proposed earlier. The magnetic moment of 1.82 B.M. is the value observed for distorted octahedral structures.[4] The following structure may therefore be suggested for the sulphate.



The zinc and cadmium sulphate as well as cadmium nitrate complexes have also been isolated with a metal–ligand ratio of 1:1 and by analogy with copper should have a similar structure. The other complexes of cadmium halides are obtained with a ratio of 1:1 and 1:2 in the anhydrous state. The coordination number four is quite common for cadmium and in order to exist as a neutral species with a tetrahedral structure the complexes must be binuclear as proposed above in the case of copper and may be formulated as C and D



C



D

The complexes VIII and X have a tetrahedral environment as in C for cadmium but IX shows that the aquated complex acquires an octahedral structure D. This shows that the tendency for both copper and cadmium is for the formation of a bridged structure. In the case of the sulphate anion a single metallic atom is favoured.

Conductivity Measurements.—It may be seen from Table 3 that the conductivity λ_m is quite high for the polynuclear compounds. This must be due to a large number of dissociating species since these values correspond with the number of ions present. The stability constant was obtained

TABLE 3.—CONDUCTIVITY OF THE COMPOUNDS IN WATER AT 25°C.

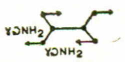
Compounds	λ	λ	α	Kion	Ks
I $[ADH(CuCl_2)_4].8H_2O$	1268	1072.00	0.8457	6.627×10^{-6}	1.509×10^{5}
II $[ADH(CuSO_4)_3].3H_2O$	1259	805.60	0.5117	2.144×10^{-4}	4.558×10^{3}
IV $[Cu_2Adipato](NO_3)_2$	574.2	248.00	0.422	1.291×10^{-7}	7.745×10^{6}
V $[(ADH)_3(CuBr_2)_4].8H_2O$	1998	1300.00	0.6506	2.845×10^{-8}	3.515×10^{7}
VI $[(ADH)_3(CuBr_2)_4].4H_2O$	2627	1789.00	0.681	1.419×10^{-8}	7.046×10^{7}
VII $[ADH\ CuSo_4].2H_2O$	424.7	247.00	0.5816	8.083×10^{-4}	1.237×10^{3}
VIII $ADH(CdCl_2)_2$	800.3	322.00	0.4025	1.09×10^{-7}	9.166×10^{7}
IX $ADH(CdBr_2)_2.4H_2O$	800.3	322.00	0.4025	1.09×10^{-7}	9.166×10^{7}
X $ADH.CdBr_2$	250.6	204.10	0.452	1.685×10^{-7}	5.936×10^{6}
XI $ADH\ Cd(NO_3)_2.2H_2O$	443.7	202.90	0.6602	6.85×10^{-7}	1.46×10^{6}
XII $ADH.Cd\ SO_4.H_2O$	593.8	214.80	0.3666	2.047×10^{-4}	4.883×10^{3}

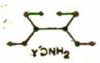
from conductivity by the method described earlier[5]. The brigded structures with more than one ligand have a higher stability than those with just one ligand. The sulphate complex with no bridging have lower stability and this supports the above conclusion that the ligand ADH favours cluster formation.

IR Spectra.—The spectra of the complexes have been characterized by comparing with those of adipic acid, hydrazine, and its derivatives,[6,7] benzoyl hydrazide[8] and the metal complexes of succindi hydrazide and malondihydrazide.[9] In the last case the absorption at 720 cm^{-1} has been attributed to the formation of H—N→M bond. In ADH this band is broad as in amines and in the complexes it is quite weak. This band has been assigned in several amides and hydrazine to ωNH_2[8] or τNH_2.

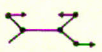
Our assignments are based on the multiplicity of the NH_2 rocking frequencies. Among the complexes this mode is shifted and is split in several ways depending on the coordinated metal atom. The pattern of splitting of these frequencies makes two broad classification which comprise the copper complexes on the one hand, and the rest of the metals studied so far viz. Co, Ni, Cd and Zn on the other. While the copper complexes have four bands at 1230, 1205, 1175 and 1160 cm,$^{-1}$ the others have only two bands at 1190 and 1140 for nickel chloride, 1175 and 1150 for cobalt chloride, 1180 and 1135 for zinc sulphate, 1120 and 1173 for cadium chloride and at 1110 and 1170 cm^{-1} for cadmium bromide. In ADH also only two bands are observed at 1230 and 1175 cm^{-1}.

In hydrazine and its mercury complexes the band at 1275 cm^{-1} is due to $\gamma\ NH_2$, that at 1098 cm^{-1} is due to $\gamma'\supset NH_2$, that at 1098 cm^{-1} is due to $\gamma'\supset NH_2$





The two bands in ADH may be assigned to the following rocking modes

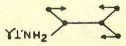


In the hydrazide complexes where bonding occurs through the amino group both the frequencies would be observed with slight shifts. In the case of bonding through the amido nitrogen, additional bands would appear due to the free amino rocking. This suggests that in copper there is a greater chance of bonding through the amido group. The rocking frequencies are known to be sensitive to the electronegativity of the environment which in the case of copper is due to the disturbance in the electrostatic charges on the metal as discussed above. The splitting might in part be related to the tendency for the reduction in electrostatic charge since the same is not true for cadmium.

Further evidence for the bonding through the amide nitrogen in copper are provided by the band at 1290 cm^{-1} which is of medium intensity here and also in ADH. It has a weak intensity in the cadmium complexes and is absent from the spectra of cobalt and nickel complexes. This has been suggested to be due to the nonplanar NH_2 twisting in the hydrazine and hydrazides.[8] This shows that the twisting mode is restricted in cases other than copper where alone the amino group is free.

The band at 985 cm^{-1} in the ADH spectrum is not found in those of the complexes but the one at 1035 cm^{-1} is shifted to higher frequencies and occurs at 1055 cm^{-1} in cadmium chloride, at 1050 cm^{-1} in cadmium bromide, 1060 cm^{-1} in zinc chloride, 1030 cm^{-1} in nickel chloride, 1040 cm^{-1} in cobalt chloride and 1075 cm^{-1} in copper chloride and bromide. This frequency has been assigned to δ NCO in acetamide.[10] In the present case this involves the bending of the N—N—C—O group. Shifts to higher frequencies indicate gain in bond order which is expected to be more for the amido group than for the amino. The large shift in the case of copper again is in accord with the participation of the amido group in coordination.

The medium intensity band at 873 cm^{-1} has been assigned in hydrazine and its complexes to ν N—N which loses intensity and is shifted to higher frequencies in the mercury complexes. In ADH this occurs at 900 cm^{-1} but is shifted to lower frequencies ~880 cm^{-1} in the complexes studied here. This might be related to the lack of resonance stabilization by the carbonyl group as the coordination is effected through nitrogen.

The 955 cm^{-1} band is another rocking mode  This absorption is shifted to higher frequencies ~960–70 cm^{-1} in the Co, Ni, Zn and $CuSO_4$ complexes but to lower ones ~950 cm^{-1} in Cu and Cd complexes. The similarity in the structure in the latter compounds might be responsible for slightly restricting this mode and hence the lower frequencies.

The rocking mode of the NH—NH_2 group provides good evidence for the bonding through either the amino or the amido. They are further supported by the C=O absorption which shifts to higher and of the N—H to lower frequencies. The structure in most cases is polymeric which shows the increasing tendency of ADH to form clusters.

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