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STUDIES ON COORDINATION COMPOUNDS

Part V.—Metallic Chloranilates

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Metallic chloranilates of the first transition series from vanadium to copper and of palladium and platinum have been prepared. They are shown to be polymers with varying degree of polymerization. The palladium, platinum, iron(III) and chromium(III) compounds are soluble in hydroxylic solvents enabling an electronic spectral study. Certain assignment of the bands have been made and it is found that chloranilic acid has the same position in the spectrochemical series as the amines. The band positions suggest a planar structure for palladium and platinum complexes and octahedral for those of iron(III) and chromium(III). The IR spectra of the chloranilates shows the M—O frequency at 530–80 cm^{-1} which increases in the same order as the Irving–Williams series.

Hydroxyquinones are known to form a variety of complex metal salts. The preparation of a series of salts of 2,5-dihydroxyquinone was reported in 1950.[1] It was argued that since the metal–ligand ratio does not change on changing the ratio of the starting material and since the analysis does not correspond to the presence of an end group, the compounds are not polymeric. Chloranilic acid has been known for a long time to form insoluble metallic salts and in the analysis of metal ions.[2] The reaction of chromic and chromous ions with chloranilic acid (CA) in alcohol has shown that in each case a product having two chromium atoms per quinone is obtained and that alcohol is oxidized to acetaldehyde.[3] Copper chloranilate is, however, a coordination polymer having a one dimensional chain structure with a degree of polymerization of 9 to 100. It has also a magnetic susceptibility characteristic of a linear chain model.[4] Bottei and Greene have isolated the CA chelates of copper, cobalt, nickel, zinc and lead and have described their thermal properties and IR spectra in a limited range. Their analytical results demonstrate the formation of coordination polymers.[5]

There are still quite a few features of the chloranilates which have not received attention, some of them being the salts of the platinum group metals, the electronic spectra of these compounds and their far infrared spectra. This paper deals with the preparation of most of the first transition series metal chloranilates and also of platinum and palladium. The far infrared spectra have been recorded to obtain the M—O frequency and the electronic spectra of the soluble salts of chromium (III), iron (III), palladium(II) and platinum(II) have been obtained. The spectra of the iron(III) compounds are not numerous and since that of FeCA is quite rich, it has been possible to assign the bands and to obtain ligand field parameters.

Experimental

The analyses were carried out by the microanalytical section of these Laboratories. IR spectra on Beckman IR-10 were kindly arranged by Professor H.C. Clark at the Department of Chemistry, University of Western Ontario, London, Canada. The electronic spectra were run on a Unicam SP-800 in the 190–700 nm range.

The compounds were prepared from barium chloranilate in dilute acetic acid. These preparations are sensitive to pH changes and hence the same was maintained above 3.5. This acidity affords greater solubility of BaCA and at the same time ensures the formation of the dianion CA^{--}. Under high acidity CAH^-, the acid chloranilate is obtained which is a disadvantage of using chloranilic acid as the starting material.

Two methods were adopted for the preparation, depending on the solubility of the metal chloride. The chlorides of chromium(IV), manganese(III), iron(III), cobalt(II), nickel(II) and copper(II) were the starting materials for method A. Other anions like Br^-, NO_3^- gave similar results.

Method A.—In each case a slight excess of metal salt was added to the solution of BaCA in dilute acetic acid. The colour of the solution which was light purple in the beginning was immediately discharged on adding the first portion of the metallic salt. The solution was kept refluxing and the cation was added slowly until the colour was no longer perceptible. The mixture was refluxed for another 2 hr. The dark coloured solids were then filtered out, washed successively with dilute acid, water, alcohol and finally with ether and dried *in vacuo*.

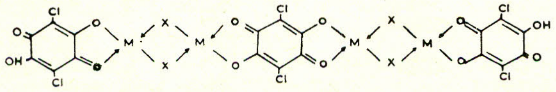
Method B.—The palladium, platinum and vanadyl complexes were prepared at lower pH because of the low solubility of their chlorides at low acidity. The BaCA was added in the right proportion and the pH was finally adjusted to 3.5.

The mixture was then refluxed for 2 hr and on cooling palladium deposited bright yellow crystals of the chloranilate. In the case of platinum the solution had to be concentrated when pale yellow crystals of the PtCA were obtained from the acidic solution. They were purified by washing with alcoholic hydrochloric acid, alcohol–ether mixture and then with ether and dried *in vacuo*.

The iron and chromium complexes were also prepared by method B. Under these conditions, the dark purple and violet black crystals of the chloranilates of iron and chromium respectively were obtained.

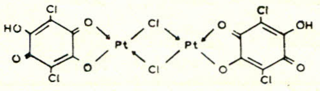
Results and Discussion

Table 1 shows the formation of two series of complexes with metal—ligand ratio of 1:1 or 2:1. CA is a strong acid with its pK_1 and pK_2 values of 0.85 and 3.18 respectively[6] which is comparable with oxalic acid and hence it is capable of displacing most of the anions from the metallic salts. Most of the transition metals studied here can be formulated as $M.CA.nH_2O$ but those by method B are of the type M_2X_2CA. It may also be observed from Table 1 that the chlorine analysis is slightly high. This may be related to the end group since one of the starting materials is the metallic chloride. In the preparations of Bottei and Greene, the carbon analysis is slightly high possibly because the starting material was the metallic acetate. On the basis of the excess chlorine, from analysis, it can be said that the degree of polymerization in the case of CuCA is 20, for MnCA $\simeq$10 and for FeCA 12. For palladium and vanadium a bridged structure is assumed in which case the degree of polymerisation is 4 with the following structure:



A

The platinum complex is probably only a dimer of the type



B

The other 1:1 complexes might have structure proposed by Bottei and Greene.[5]

IR Spectra.—The spectra of these complexes have very few bands as compared with chloranilic acid. However, in the 600–250 cm^{-1} region, the former have more absorptions than the latter. A correlation of these spectra has been attempted here on an empirical basis and the assignments in Table 2 are only qualitative.

The νC—O frequency occurring in CA at 1630 and 1670 cm^{-1} is shifted to considerably lower frequencies ~ 1480–1530 cm^{-1} in all the complexes except that of platinum where the shift is to higher frequencies. The second C—O frequency occurs in the other carbonyl compounds at 1355–80 cm^{-1}. PtCA has a very strong absorption here and this one is shifted to lower frequencies compared with CA. A shift to lower frequencies is characteristic of the loss of carbonyl character which supports the polymeric structure proposed for the chloranilates.[5] The behaviour of platinum is justified by structure B where both types of absorptions are expected. The shift to higher frequencies show that the carbonyl group is not actively participating in complex formation. Furthermore because of the low degree of polymerization it is possible to observe the end group absorptions.

Some of the absorptions in CA are lost on complex formation and these may be assigned to the vibrations due to the OH group. These are the strong bands in the 1200–1300 cm^{-1} region which have been assigned to the δ(OH) in-plane and ν(C—O) together with δ′(OH) in-plane bands in the hydroxyquinones.[7] The γ(OH) vibration occurring in the latter compounds at 770 cm^{-1} is also noted in CA but is lost in the complexes.

The medium intensity bands at 850 ± 10 and 1000 ± 20 cm^{-1} in the CA and its complexes suffer only minor shifts. The C—Cl absorption has been noted in tetrachloroethylene at 957 cm^{-1} and at 1025 cm^{-1} in 2,5-dichlorobenzoquinone[8] and hence the band at 1000 cm^{-1} is assigned similarly. The 850 ± 10 cm^{-1} band has been assigned to the C—O bending mode. The absorption at 700 cm^{-1} in chloranil and other chloroquinones is attributed to the ring breathing mode.[8] In CA it occurs as a weak band at 695 cm^{-1} but it is not noted in the complexes at this frequency. A band, however, appears in the MCAs at 630–50 which is rather lower for ring breathing but is more appropriate for the αC—C absorption or a combination of both. The 580–90 cm^{-1} region is the range for coordinated water. Since all the complexes are strongly aquated and since absorptions in the 3300 and 1600 cm^{-1} also indicate the OH vibrations due to water, this frequency is accordingly assigned.

There is no absorption in the 590–400 cm^{-1} region in either CA or the chloroquinones. The complexes, on the other hand, have a weak to medium intensity band at 530 and in some cases also at 470 cm^{-1}. This is the region for the νM—O frequency and the spectra do indicate systematic shifts similar to the metallic oxalates and acetylacetonates.[9] Here the M—O frequency is found at 534, 540 for VCA; 530, 550 for CrCA; 562 for MnCA and FeCA; 560 for CoCA and NiCA; 565 for CuCA; 560 for PdCA and at 580 and 520 for PtCA. There is a systematic gain in frequency as the series is ascended. Simultaneously with this, the ν(C=O) is also altered. In man-

TABLE 1.—ANALYTICAL RESULTS.

Complex	Colour	C		H		Cl	
		Calc	Obs	Calc	Obs	Calc	Obs
$(VO)_2(CA)_2Cl.10H_2O$	dark green	18.84	18.60	2.62	2.43	23.30	23.18
$Cr(CA).3.5H_2O$ (Insoluble)	black	22.36	22.31	2.17	2.31	22.05	22.45
$Cr_2(CA).Cl_{3\cdot2}.7H_2O$ (Soluble)	dark violet	13.09	13.23	2.54	2.70	33.45	33.19
$Mn(CA).Cl_{0\cdot2}3H_2O$	dark brown	22.27	22.85	1.85	1.94	24.20	24.15
$Fe(CA).Cl_{0\cdot25}.1.5H_2O$	dark violet	24.08	23.84	1.01	1.12	26.75	26.62
$Co(CA).3.5H_2O$	dark brown	21.88	21.58	2.13	1.90	21.69	22.33
$Ni(CA).3.5H_2O$	dark green	21.90	21.90	2.13	2.44	21.60	21.99
$Cu(CA).Cl_{0\cdot1}10.5H_2O$	dark green	25.40	25.72	0.35	0.53	26.30	26.76
$Pd_2(CA)Cl_2.5H_2O$	yellow	12.41	12.06	1.72	1.96	24.49	24.24
$Pt(CAH)Cl.H_2O$	yellow	15.78	15.60	0.66	0.93	15.57	15.52

TABLE 2.—IR SPECTRAL BANDS AND THEIR ASSIGNMENT.

CA	VOCA	CrCA	MnCA	FeCA	CoCA	NiCA	CuCA	PdCA	PtCA	Assignment
3500	3440	3540	3640	3340	3480	3560	3500	3600	3540	νO—H
3240	3350	3460	3540		3420	3410		3540	3400	
					3320			3400	3320	
1670ssh									1690vs	
1630vs	1620m	1620s			1590m		1620w	1650w	1655vs	ν_{as}C=O
	1580m		1580s					1620m		
1520wsh		1530vs	1500vs	1530vs	1490vs	1500vs			1520s	ν_{as}C—O
	1480vs		1480vssh			1490vs	1490vs	1500vs		
1370s	1360vs	1355s	1380s	1370s	1380s	1380vs	1360m	1355vs	1360vs	ν_sC=O
1280vs	1310w		1280w	1305m	1320w	1310w	1310m	1270m		ν_sC—O
1265vs		1270w						1260w		
1210m										
1175w									1175w	
				1030m						
990s	980w	1010	995w	1000w	1010w	1000w	1000w	980w	980m	νC—C1
850m	860m	860s	845m	852m	850s	855m	855m	835m	860m	δC—O
	840m									νV=O
760w										γO—H
695w	625w	630s	620m	620m	655 } s	615w	625w		655w	ring breathing
					645 }					αC—C—C
		585m	585m	590msh				580sh	580m	Coordinated water
575m	570m	550m	562m	562m	560s	560m	565m	560s		νM—O
	535 } m	530m					540sh		520m	
	540 }						530m			
390w	460w	470m	465w	490m	480m	495m	460w		}	δC—O our of
	405w	440w		435w	440w	432w		410w	420w }	plane
		395m	385m	410w	400m				380m }	+ νM—O
340m	350m	330m	320m	310mbr	340w	320w	350m	360m	350m	M—C1
		320w								
280w		290w	260w	280br	300w		255m	270mbr	310 } m	ring
									300 }	deformation

vs—very strong; m—medium; w—weak; br—broad; sh—shoulder.
The spectra were all run using KBr pellets.

ganese, iron, cobalt and nickel where the M—O frequency is on the higher side, the ν_s(C=O) also occurs at a comparatively higher position ~1380 cm^{-1}. In the other complexes with lower M—O frequency, the ν(C = O) is also lower. These assignments are consistent with the spectra of the metallic oxalates particularly in view of the similarity of their acidity. The variation in the M—O frequency places the metals in the following order for the first transition series. $V < Cr < Mn,Fe,Co,Ni < Cu$. This is the Irving–Williams series also followed by the acetylacetonates.[10] The Pt—O frequency is split into those at 520 and 580. Since PtCA has only one molecule of water according to the analysis, the strong absorption is more consistent with a Pt—O absorption. The bridging in the platinum, palladium and vanadium compounds is also supported by the M—Cl (bridging) for planar chain structures near 350 cm^{-1}.[11]

The 390 cm^{-1} band in CA is assigned to β(C=O) in chloroquinones. This should be susceptible to changes on complex formation. Quite a few bands, however, occur in this region for the complexes which makes even a tentative assignment quite difficult.

Electronic Spectra.—Spectra of most of these complexes could not be recorded because of their insolubility in practically all the solvents. The complexes of Fe(III), Cr(III), Pd(II) and Pt(II) are, however, soluble and the spectra have certain interesting features. The acid is reported to absorb at 18870 and 30120 cm^{-1}.[6] In methanol it absorbs at 46300 cm^{-1}, has a diffuse doublet at 30860 cm^{-1} and 29940 cm^{-1} and a broad band at 20620 cm^{-1}. The complexes mentioned above have the first band at 44600–45200. A red shift in the complexes shows the removal of proton and delocalization of the lone pair on the oxygen into the benzenoid ring. The diffuse doublet at 30860 and 29940 cm^{-1} in CA must be related to the π→π* transition and to the presence of charged as well as neutral species. It may be mentioned that CA absorbs at 30200 cm^{-1} at pH 3.8 and at 32600 cm^{-1} at pH 1.5.[12] The absorption of the complexes in this region should, therefore, reveal the type of species in the molecule. It may be seen from Table 3 that palladium(II) has a band at 32420, iron(III) and chromium(III) at 31950 and platinum at 30770 cm^{-1}. In accordance with these relative shifts the above metals are arranged in the decreasing order of covalence. This implies a larger ionic character for platinum. From structure B and the IR spectra also the platinum complex is supposed to be ionic in characrer.

The spectrum of the iron complex is dominated by broad bands due to internal ligand and/or charge transfer bands. The following bands occur in the spectrum 45050, 41320 sh, 31950 broad, 26390, 21550 sh, 20200 and 17180 broad. In [Fe (trifluoroacetate)$_3$]^{III}, the bands at 17.9 and 21.3 kK have been assigned to the $^6A_g \rightarrow {^4T_2}_g(G)$ and $^6A_{1g} \rightarrow {^4E_g}$, $^4A_{1g}(G)$ transitions.[13] There is a significant similarity here with trifluoroacetate in that the 21550 and 17180 cm^{-1} bands lie on the broad maximum of the CA ion which itself absorbs at 20200 cm^{-1}. In the trisoxalate the former band is noted at 22200 cm^{-1} and hence there is an empirical justification for the assignment of the two bands to the same absorptions.

The band at 26390 cm^{-1} has a high intensity and is not a d–d transition. The band at 31950 mentioned earlier is also of high intensity and both of these should be charge transfer bands. It is possible to calculate the transition energies of the CT absorptions by the method of Lintvedt and Kernitsky.[14] The 26390 and 21550 cm^{-1} bands in FeCA are in the range of $t_{2g} \rightarrow \pi^*$ and $\pi \rightarrow e_g$ transitions in the [Fe (acac)$_3$]. III According to these authors the sum of $(\pi\text{-}t_{2g}) + (t_{2g}\text{-}e_g) + (e_g\text{-}\pi^*)$ will give the π→π* transition located on the ligand. Assuming that the band at 17180 is a $^6A_{1g} \rightarrow {^4T_{2g}}$ transition, a comparison with the Tanabe–Sugano diagram gives a Δ value of 17220 cm^{-1} and B=820 cm^{-1}. Substituting this value of Δ into the equation, $\Delta = f(\text{ligand})g(\text{metal})$, the value of $f = 1.25$ is obtained which is similar to those of ammonia and ethylenediamine.[15] With this value of f and a value of B=820 cm^{-1}, B=66% is obtained which is expected of the covalent nature of Fe(III) compounds. Finally, proceeding by the method of Lintvedt and Kernitsky, it is found that a value of 30760 cm^{-1} is obtained for the π→π* transition which is 1190 cm^{-1} short of the observed energy viz. 31950 cm^{-1}. This difference is of the same order as for the acac complexes.[14] The assignment of the various bands is thus neatly substantiated and it is possible to say that the 21550 and 26390 bands are due to charge transfer.

TABLE 3.—ELECTRONIC SPECTRA OF THE METALLIC CHLORANILATES.

Compound	Max (cm^{-1})	log	Assignment
Pt(CAH)C1.H_2O	25000	2.22	d–d
	27030	2.28	d–d
	30770	2.61	$\pi \rightarrow \pi^*$
	40000	3.11	$\pi \rightarrow e_g^*$
	44840	3.32	$n \rightarrow \pi^*$
Pd CAC1 .5H_2O	28570	2.13	$^1A_1 \rightarrow {^1E_g}$
	32420	2.93	$\pi \rightarrow \pi^*$
	37450	3.42	$\pi \rightarrow e_g^*$
	43480	3.61	$\sigma \rightarrow e_g^*$
	44640i	3.34	$n \rightarrow \pi^*$
Cr (CA)C1 .7H_2O	20000	2.18	Intraligand
	28570	2.90	$^4A_{2g}(F) \rightarrow T_{1g}(F)$
	29590i	2.86	$^4A_{2g}(F) \rightarrow {^4T_{1g}}(P)$
	31900	2.73	$\pi \rightarrow \pi^*$
	4380i	3.82	$\sigma \rightarrow e_g^*$
	45250	3.92	$n \rightarrow \pi^*$
FeCA.H_2O	17180	2.18	$^6A_1 \rightarrow {^4T_2}$
	20200	2.19	Intraligand
	21550	2.18	$\pi \rightarrow e_g$
	26390	2.44	$t_{2g} \rightarrow \pi^*$
	31950	2.70	$\pi \rightarrow \pi^*$
	41320i	3.53	$\sigma \rightarrow e_g^*$
	45050	4.18	$n \rightarrow \pi^*$

i inflexion

The high energy and high intensity absorptions at 41320 and 45050 should be due to charge transfer. The latter has already been assigned to the ligand n→π* transition while the former falls in the range of $\sigma \rightarrow e_g^*$ transition.

The spectrum of the chromium complex again consists of shoulders and has very weak absorptions in the visible region. The complex absorbs at 28570, 29590 sh, 31900 sh, 43860 sh and 45250 cm^{-1} and a very weak absorption at 20000 cm^{-1}. Proceeding with the values of f(ligand)$=1.25$, obtained above and with $g(\mathrm{Cr}^{3+}) = 17$[15], Δ is calculated to be 21250 cm^{-1} which is consistent in comparison with the Cr^{3+} and Fe^{3+} values.[15] These further yield $B = 704$ cm^{-1} and $\beta = 68.5\%$. Using these values in the Tanabe–Sugano diagrams the following assignments can be made.

${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$	28160 cm^{-1}
${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	44100 cm^{-1}

The band at 28570 cm^{-1} is therefore due to the ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition which occurs at 24000 cm^{-1} in the hexaaquo complex where the value is also 70%.[15] Similar is the case with the ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition to which the shoulder at 43860 cm^{-1} is assigned. Both of these transitions have a comparable magnitude in the trifluoacetate complex of chromium(III). Furthermore, the calculated and observed values seem to be in good agreement.

The other bands at 29590 and 31900 cm^{-1} may be assigned to the ligand $\pi \rightarrow \pi^*$ charge transfer. The latter is similar to the band in the iron complex. The 45050 cm^{-1} band which has been discussed earlier is also assigned to $n \rightarrow \pi^*$ transition by analogy.

Platinum(II) complexes have been shown to have three main absorptions. For $\mathrm{PtCl_4}^{2-}$ the band positions are $b_{2g}(x,y) \rightarrow b_{1g}(x^2\text{-}y^2)$ (${}^1A_{1g} \rightarrow {}^1A_{2g}$) at 25000 cm^{-1}, the $e_g(xx_1y_2) \rightarrow b_{1g}(x^2—y^2)$ (${}^1A_{1g} \rightarrow {}^1E_g$) at 29700 cm^{-1} and $a_{1g}(z^2) \rightarrow b_{1g}(x^2—y^2)$ (${}^1A_{1g} \rightarrow {}^1B_{1g}$) at 37000 cm^{-1}. Charge transfer bands have been observed: $L_\pi \rightarrow d\sigma^*$ at 43670 and 46300 and $L\sigma \rightarrow d\sigma^*$ at 50000 cm^{-1}.[16,17] In a series of complexes with σ and π donor ligands it has been found that the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ band shifts to higher frequencies in the case of π bonding ligands and is lower for σ bonding ones.[18,19]

Platinum chloranilate has absorptions at 25000, 27030 sh, 30770, 40000 and 44840 cm^{-1}. Out of these the 44840 cm^{-1} has already been assigned to the ligand $n \rightarrow \pi^*$ transition. The band at 30770 cm^{-1} is again the $\pi \rightarrow \pi^*$ intraligand absorption and has also been discussed. Out of the remaining three the one at 40000 cm^{-1} is fairly strong and hence is also assigned to charge transfer. The position of this band compared with $\mathrm{PtCl_4}^{2-}$ is possibly modified due to the nature of the ligand CA. Chloranilic acid by nature should have good σ and π donor properties. The participation of the quinonoid grouping makes it a good π donor ligand but in the platinum compound it is reduced to a certain extent as indicated by the red shift of the $\pi \rightarrow \pi^*$ absorptions corresponding to the CA. The σ donor properties are therefore more marked here. It has been shown earlier that the ligand field parameters for iron and chromium place this ligand at the same position as the amines. However, this is modified in the case of platinum because of the participation of chlorine as in structure B. Lower values for the different transitions will therefore be expected as in trans $[\mathrm{PtCl_2(n\text{-}octyl_2NH_2)_2}]$ which has absorptions at 26400, 31200 and 37000 cm^{-1} or trans$[\mathrm{PtCl_2(cyclopentyl_2NH)_2}]$ which has an identical spectrum.[18,19] It is clear from a comparison with these spectra that the 25000 and 27030 cm^{-1} bands are d–d transitions but a definite assignment is difficult at this stage. The 40000 cm^{-1} band may, however, be assigned to ligand→metal $\sigma \rightarrow e_g^*$ transition for which a red shift is noted in the palladium complex.

The spectrum of PdCA consists of bands at 28570 sh, 32420, 37450, 43480 and 44640 cm^{-1}. The 32420 cm^{-1} and the 44640 cm^{-1} bands have been discussed above and related to $\pi \rightarrow \pi^*$ intraligand and $n \rightarrow \pi^*$ charge transfer transitions respectively. The band at 37450 cm^{-1} is assigned to $L \rightarrow M\pi \rightarrow e_g^*$ transition noticed in the platinum complex at 40000 cm^{-1}. This shift compared with platinum is quite small and the Pt—Pd ratio is 1.06:1. For a d–d transition this ratio is usually 1.22:1. The intensity is, however, high for a d–d transition. This band is, therefore, assigned to $L \rightarrow M\pi \rightarrow e_g^*$ charge transfer. These charge transfer bands are easily possible in a system like the chloranilates where the ligand has a high electronegativity as well as a π electronic system and both of these conditions are ideal for charge transfer.

The band at 28570 is weak in intensity and is assigned to ${}^1A_{1g} \rightarrow {}^1E_g$ transition. The corresponding bands in $\mathrm{PdCl_4}^{2-}$, $\mathrm{PdBr_4}^{2-}$ and $\mathrm{Pd(NH_3)_4}^{2+}$ are observed at 21000, 19600 and 33800 cm^{-1}.[17] The assignment of this transition is in line with the nature of the ligand and its similarity with the amines in the spectrochemical series. Slight modifications due to the participation of chlorine are, however, possible and this might be the reason for the observed position.

The complexes of both platinum and palladium have spectra similar to square planar complexes. The spectra of iron and chromium complexes on the other hand are related to octahedral structure. The position of chloranilic acid in the spectrochemical series is almost the same as those of the amines in the four soluble chloranilates studied here.

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