

Physico-Chemical Studies on the Mixed Ligand Complexes of Chromium(III) Nitrilotriacetate with Some Phenols and Phenolic Acids

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On the basis of conductance, polarographic, magnetic, ir and electronic spectral studies, the complexes of the type $K_2[Cr(NTA)(P)_2]$ and $K_2[Cr(NTA)(A-A)]$ (P=deprotonated phenol, 4-chlorophenol, 4-nitrophenol, *o*-cresol, hydroquinone or α -naphthol; A-A=pyrogallol, pyrocatechol, alizarin, salicylic acid, 4-aminosalicylic acid or 4-sulphosalicylic acid) were found to have an octahedral structure. The coordinating power of these phenolic compounds was in the order hydroquinone > 4-nitrophenol > phenol = 4-aminosalicylic acid > 4-chlorophenol = pyrogallol = pyrocatechol = *o*-cresol = salicylic acid = 4-sulphosalicylic acid > α -naphthol > alizarin.

CHROMIUM(III) and its compounds occurring in brewers yeast and other foods are found to be of outstanding biological activity¹, acting as a cofactor in initiation of insulin and facilitating the initial insulin tissue interaction forming ternary complexes. The ternary complexes of chromium nitrilotriacetate (NTA) with acetylacetone, phenanthroline, dipyriddy, oxalate, halide ions²⁻⁴, amino acids⁵ and heterocyclic amines⁶ have been studied in relation to their preparation, stability, magnetic and ir spectra. The present communication deals with the preparation and characterisation of mixed ligand complexes of chromium(III) with NTA as primary and phenolic compounds as secondary ligands in order to know the coordinating capacity of NTA and comparative ligand field parameters of phenolic compounds. These complexes also may be of biochemical, industrial and analytical importance.

Experimental

All the chemicals used were of B.D.H., A.R. grade and the solutions were prepared in distilled water. Physical measurements were made by the methods reported earlier^{5,6}.

Preparation of the complexes: Ammonium hydroxonitrilotriacetatoaquochromate(III) dihydrate, $NH_4[Cr(OH)NTA(H_2O)] \cdot 2H_2O$ (I), prepared by the method of Uehara *et al*⁸ was used as a starting material for the preparation of all the complexes.

Potassium nitrilotriacetatobis-(phenolato)chromate(III):

$K_2[Cr(NTA)(P)_2]$: P=deprotonated phenol, 4-chlorophenol, 4-nitrophenol, *o*-cresol, hydroquinone or α -naphthol. Solutions of I and phenol in water and alcohol, respectively were mixed in the 1 : 3 mole ratio and pH of the mixture was raised to

9.0 by the addition of KOH. The mixture was then refluxed on water bath for about 2 hr and cooled in ice. An excess of alcohol was then added till the purple or violet crystals separated out, which were filtered, recrystallised from a small quantity of water and then dried in a vacuum desiccator over silica gel. The complexes were soluble in water and fairly stable.

Potassium nitrilotriacetato (phenolato or phenolic acido)chromate(III):

$K_2[Cr(NTA)(A-A)]$: A-A=pyrogallol, pyrocatechol, alizarin, salicylic acid, 4-aminosalicylic acid or 4-sulphosalicylic acid, (all deprotonated). These were similarly prepared mixing one mole of I and one mole of A-A.

Chemical analysis, magnetic moments and molar conductances in water of the complexes prepared are given in Table 1.

Results and Discussion

The three spin allowed transitions were obtained in the electronic spectra of the complexes in solid state and also in aqueous solutions with the same wave numbers in both the cases, indicating no structural changes in solution. The assignments of these transitions and the methods of calculation for finding out the values of 10 Dq, B and $\beta_{3,5}$ were the same as reported earlier⁵.

Table 2 shows that the deviation $|\delta v_{2,3}|$ of the calculated transition energies according to procedures (a), (b) and (c) is of the order of a few percent and decreases according to $|\delta v(b)| > |\delta v(a)| > |\delta v(c)|$. Therefore, it is concluded that out of the numerical procedures applicable in the spectra of the octahedral chromium(III) complexes, the best

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TABLE 1—ANALYTICAL DATA OF THE COMPLEXES

Sl. No.	Complexes	Analysis % ; Found/(Calcd.)			# _{eff} (B.M.)	Molar conductance* (mhos)
		Metal	Carbon	Hydrogen		
1.	K ₂ [Cr(NTA)(C ₆ H ₄ O ₂) ₂]	9.69 (9.74)	40.49 (40.45)	2.96 (2.99)	3.69	230
2.	K ₂ [Cr(NTA)(C ₆ H ₄ O ₂ N) ₂]	8.70 (8.75)	36.21 (36.36)	2.34 (2.36)	3.70	229
3.	K ₂ [Cr(NTA)(C ₆ H ₄ O) ₂]	10.25 (10.32)	42.58 (42.86)	3.14 (3.17)	3.70	300
4.	K ₂ [Cr(NTA)(C ₇ H ₅ O ₂ N)]	11.01 (11.09)	33.37 (33.26)	2.33 (2.35)	3.71	228
5.	K ₂ [Cr(NTA)(C ₆ H ₄ OCl) ₂]	9.03 (9.09)	38.03 (37.78)	2.42 (2.45)	3.95	225
6.	K ₂ [Cr(NTA)(C ₆ H ₄ O ₂) ₂]	9.16 (9.22)	25.68 (25.53)	1.75 (1.77)	4.01	300
7.	K ₂ [Cr(NTA)(C ₆ H ₄ O ₂) ₂]	12.07 (12.15)	33.83 (33.64)	2.31 (2.34)	4.00	300
8.	K ₂ [Cr(NTA)(C ₇ H ₇ O) ₂]	9.68 (9.77)	44.89 (45.11)	2.60 (2.63)	3.98	240
9.	K ₂ [Cr(NTA)(C ₇ H ₄ O ₂) ₂]	11.39 (11.45)	34.63 (34.36)	2.28 (2.20)	4.05	290
10.	K ₂ [Cr(NTA)(C ₇ H ₄ O ₂ S)]	9.70 (9.76)	29.45 (29.27)	1.68 (1.69)	3.99	300
11.	K ₂ [Cr(NTA)(C ₁₀ H ₇ O) ₂]	8.57 (8.61)	51.24 (51.65)	3.27 (3.31)	4.10	250
12.	K ₂ [Cr(NTA)(C ₁₄ H ₈ O ₄) ₂]	9.29 (9.35)	43.00 (43.16)	2.13 (2.16)	4.15	235

* 0.001 M solutions in water were prepared for conductance measurements (cell constant=1.12).

TABLE 2—ELECTRONIC SPECTRAL DATA AND CALCULATED TRANSITION ENERGIES (cm⁻¹)

Complex no.*	Method of calculation	⁴ A _{2g} → ⁴ T _{2g}	⁴ A _{2g} → ⁴ T _{1g} (F)	⁴ A _{2g} → ⁴ T _{1g} (P)	B	β _{2,2}	δν (cm ⁻¹)	δν (%)	L.F.S.E k cal mole ⁻¹	E _{1,2} (±0.02)
1.	expt	17500	24500	38000						
	(a)	10 Dq	fitted	38500	700	0.76	+500	1.30		60.00
	(b)	10 Dq	23955	fitted	630	0.68	-545	2.25		
2.	(c)	10 Dq	24240	38250	666	0.72	±255	0.85		59.53
	expt	17363	26000	38500						
	(a)	10 Dq	fitted	40430	956	1.04	+1930	4.77		
3.	(b)	10 Dq	24591	fitted	733	0.79	-1409	5.56		
	(c)	10 Dq	15231	39263	827	0.90	±766	2.49		58.28
	expt	17000	24000	37000						
4.	(a)	10 Dq	fitted	37605	707	0.77	+605	1.61		
	(b)	10 Dq	23375	fitted	625	0.68	-625	2.63		
	(c)	10 Dq	23694	37295	666	0.72	±300	1.03		58.28
5.	expt	17000	24500	37200						
	(a)	10 Dq	fitted	38175	778	0.85	+974	2.55		
	(b)	10 Dq	23595	fitted	653	0.71	-906	3.76		
6.	(c)	10 Dq	24045	37655	713	0.78	±454	1.54		56.57
	expt	16500	23500	35450						
	(a)	10 Dq	fitted	36725	715	0.77	+1275	3.53		
7.	(b)	10 Dq	22120	fitted	538	0.58	-1378	5.86		
	(c)	10 Dq	22870	36080	630	0.68	±629	2.24		56.57
	expt	16500	24000	37000						
8.	(a)	10 Dq	fitted	37340	789	0.85	+338	0.90		
	(b)	10 Dq	23725	fitted	748	0.81	-273	1.15		
	(c)	10 Dq	23850	37145	766	0.83	±148	0.50		56.57
9.	expt	16500	24000	36400						
	(a)	10 Dq	fitted	37355	789	0.85	+938	2.51		
	(b)	10 Dq	23195	fitted	673	0.73	-804	3.40		
10.	(c)	10 Dq	23585	36815	726	0.79	±417	1.44		56.57
	expt	16500	23500	36350						
	(a)	10 Dq	fitted	36725	715	0.77	+375	1.02		
11.	(b)	10 Dq	23145	fitted	666	0.72	-355	1.52		
	(c)	10 Dq	23320	36530	690	0.75	±179	0.62		56.57
	expt	16500	23500	36100						
12.	(a)	10 Dq	fitted	36725	715	0.77	+625	1.70		
	(b)	10 Dq	22895	fitted	633	0.68	-606	2.60		
	(c)	10 Dq	23195	36395	673	0.73	±301	1.05		56.57

(Table 2 Contd.)

10.	expt	16500	23800	36800					56.57	0.68
	(a)	10 Dq	fitted	37085	759	0.82	+ 284	0.76		
	(b)	10 Dq	23565	fitted	724	0.78	- 273	0.99		
11.	(c)	10 Dq	23675	36925	740	0.80	± 127	0.43		
	expt	16200	23800	34900					55.54	0.65
	(a)	10 Dq	fitted	36995	813	0.88	+ 2094	5.66		
12.	(b)	10 Dq	21837	fitted	542	0.59	- 1963	8.50		
	(c)	10 Dq	22865	35830	673	0.73	± 932	3.33		
	expt	16000	23700	35400					54.85	0.63
	(a)	10 Dq	fitted	36830	835	0.91	+ 1428	3.87		
	(b)	10 Dq	22590	fitted	666	0.72	- 1108	4.90		
	(c)	10 Dq	23110	35995	740	0.80	± 593	2.10		

*Complex numbers are the same as in Table 1.

TABLE 3—IR DATA (cm⁻¹) AND THEIR ASSIGNMENTS

Complex no.*	-COOH	-COO-Cr	-COO ⁻	M-N and M-O	ν^{**} C-H	δ^{**} C-H	Comple- ments**
NTAH ₂	1669 vs 1233 m						
NTA(NH ₂) ₂			1623 vs				
1.		1620 s, 1470 s		520 m, 400 w	1300 m, 1200 m 1050 w	950 m, 800 m 600 w	3350 m
2.		1600 s, 1380 s		520 s, 400 w	1080 m, 1040 m 1000 w	900 s, 740 s 600 m	1530 m 1350 m
3.		1600 s, 1400 s		520 s, 400 w	1100 m, 1000 m	940 m, 920 m 740 w	—
4.		1620 s, 1450 s		520 m, 360 b	1300 m, 1250 m 1150 w	950 s, 900 m 700 w	3400 m
5.		1600 s, 1380 s		500 m, 400 w	1200 m, 1140 s 1000 s	900 s, 740 m 600 m	700 s
6.		1620 s, 1490 s		540 s, 380 w	1100 w, 1040 m	950 s, 750 s 600 s	3400 b
7.		1600 s, 1470 s		540 s, 450 w	1300 m, 1200 m 1150 m	950 w, 900 m 700 w	—
8.		1600 s, 1400 s		520 s, 400 w	1120 m, 1020 m	850 w, 700 m 600 w	—
9.		1640 s, 1420 s		520 s, 400 w	1120 s, 1050 w 1000 w	910 s, 750 m 620 s	—
10.		1640 s, 1480 s		540 w, 360 w	1260 m, 1040 w	920 m, 840 m	1155 m, 700 m
11.		1600 s, 1480 s		520 m, 400 w	1120 m, 1040 m	900 s, 740 m 620 w	—
12.		1600 s, 1460 s		520 m, 400 b	1300 m, 1210 m 1100 m	950 m, 900 m 700 w	—

* Complex numbers are the same as in Table 1 ; **The absorption arising from secondary ligands ; s = strong, m=medium, b = broad and w = weak.

fit for the transitions ν_2 and ν_3 can be achieved by using the method (c). In the present compounds, the deviation $|\delta v(b)|$ resulting from method (b) is very large, thus reflecting the uncertainty in the energy of the third band, ν_3 . Evidently, if ν_3 is employed in the fit, $|\delta v_3|$ (in percent) is smaller than $|\delta v_2|$ which results if ν_3 is used. Finally in the method (c) $|\delta v_2| = |\delta v_3|$. Therefore, within the approximation of the three parameter ligand field theory, the energies of both the second and third bands (ν_2 and ν_3) are reproduced equally well. In addition, there does not exist a misfit of ν_3 which could be redistributed on ν_2 and ν_3 , if method (c) is applied. If these were true, a value of $|\delta v|$ intermediate between $|\delta v(a)|$ and $|\delta v(b)|$ would be expected. However, $|\delta v(c)|$ is always smaller than both $|\delta v(a)|$ and $|\delta v(b)|$ (Table 2).

The observed values of 10 Dq reveal that the ligand field strength of secondary ligands are in the order hydroquinone > 4-nitrophenol > phenol = 4-

aminosalicylic acid > 4-chlorophenol = pyrogallol = pyrocatechol = o-cresol = salicylic acid = 4-sulphosalicylic acid > α -naphthol > alizarin. This order of coordinating power is also reflected from the $E_{1/2}$ values, taken from the polarograms of 0.001 M solutions of the complexes (pH=6.5). The effect of varying ligand field strength seems to be reflected also in the magnetic moments of the complexes e.g. chlorophenol, pyrogallol, pyrocatechol, etc. in which the average ligand field strength is weak and have values = 3.95-4.15, whereas hydroquinone, 4-nitrophenol, phenol and 4-aminosalicylic acid having a greater ligand field have a moment of only ~3.70 B.M. These values of magnetic moment are close to the spin only values for octahedral complexes of chromium(III). The molar conductance values indicate the presence of three ions in the complexes.

The same information regarding the coordinating capacity of phenols and phenolic acids, arranged in

the above order, is also derived from the values of $\beta_{3,8}$ for their respective complexes.

IR spectra: The bands obtained in the IR spectra of the ligands and their complexes are given in Table 3. The uncoordinated COO^- stretching bands obtained at 1669 and 1233 cm^{-1} shift towards lower and higher side, respectively in the spectra of complexes. Hence the bands in the ranges 1600-1640 and 1400-1490 cm^{-1} are due to coordinated carboxyl groups. Tomito and Ueno⁷ also observed the tetradentate nature of NTA in the transition metal complexes.

A comparison of the spectra of free ligand and their respective complexes reveals the disappearance of the band at 3400 cm^{-1} (free ligand) indicating the loss of phenolic proton on complexation forming metal oxygen link. The extra bands at 3400 cm^{-1} in the spectra of complex no. 1, 4 and 6 due to uncoordinated OH, NH_2 and OH, respectively, at 1530 and 1350 cm^{-1} in the spectrum of the 2nd

complex due to C-NO₂, 700 cm^{-1} in the spectrum of the 5th complex due to C-Cl and at 1150 and 700 cm^{-1} in the spectrum of the 10th complex due to C-SO₃ were obtained. The bands observed at about 520 and 400 cm^{-1} may be attributed to either M-N or M-O bond.

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