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**Cr(III) Complexes of Salicylic,
Thiosalicylic & Thioglycollic Acids,
m-(Mercaptoacetamido)phenol &
p-(Mercaptoacetamido) chlorobenzene**

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Cr(III) complexes with salicylic acid (SA), thiosalicylic acid (TSA), thioglycollic acid (TGA), *m*-(mercaptoacetamido)phenol (*m*-MAP) and *p*-(mercaptoacetamido)chlorobenzene (*p*-MCB) have been prepared. Their electronic spectral data have been analysed to calculate 10 *Dq*, CFSE, *B* and β values. Value of *B* (less than 1) is indicative of strong *d* π -*p* π interactions. Based on 10 *Dq* values, the ligands have been arranged in a nephelauxetic series.

THE formation constants of Cr(III) complexes of salicylic acid (SA), thiosalicylic acid (TSA), thioglycollic acid (TGA), *m*-(mercaptoacetamido)phenol (*m*-MAP) and *p*-(mercaptoacetamido)chloro-

benzene (*p*-MCB) were reported earlier by us¹. The solid complexes have now been isolated and their ligand field parameters determined.

All chemicals used were BDH (AR) reagents. The ligands *m*-MAP and *p*-MCB were prepared by adopting the method described previously².

The electronic absorption measurements in solution were made with Bausch and Lomb spectronic 20 spectrophotometer using acetone as the solvent.

Keeping in view the analytical data (Table 1) and known preference of Cr(III) for octahedral symmetry, the present complexes can be assigned octahedral stereochemistry which finds further support from electronic spectral data. Cr(III) has 3*d*³ electronic configuration with ⁴*A*_{2g} ground state. In octahedral field three transitions,

$${}^4A_{2g} \rightarrow {}^4T_{2g} (F), {}^4A_{2g} \rightarrow {}^4T_{1g} (F) \text{ and } {}^4A_{2g} \rightarrow {}^4T_{1g} (P)$$

are expected. These normally occur around 600, 400 and 270 nm respectively. In some cases, in addition to these bands, a spin-forbidden band, due to the transition ²*E*_g ← ⁴*A*_{2g} also occurs. In the present case two broad bands are observed around 600 and 400 nm with the indication of the third band below 340 nm, the calculated value of which is recorded in Table 2. Because of the weak character of the transition of ²*E*_g ← ⁴*A*_{2g} we could not observe the fourth band.

Assuming *O*_h symmetry, 10 *Dq* has been directly derived from the first spin allowed band following the procedure of Orgel³. From 10 *Dq*, CFSE values for various Cr(III) complexes have been

TABLE 1 — ANALYTICAL DATA OF Cr(III) COMPLEXES

Complex	Composition	Cr (%)		S (%)	
		Found	Calc.	Found	Calc.
Cr(III)-SA	Cr(C ₇ H ₄ O ₃) ₂ Na.2H ₂ O	13.47	13.58	—	—
Cr(III)-TSA	Cr(C ₇ H ₄ O ₂ S) ₂ Na.2H ₂ O	12.44	12.53	15.38	15.45
Cr(III)-TGA	Cr(C ₂ H ₃ O ₂ S) ₂ Na.2H ₂ O	17.75	17.86	21.97	22.04
Cr(III)- <i>m</i> -MAP	Cr(C ₈ H ₈ O ₂ SN) ₂ Cl.2H ₂ O*	10.60	10.67	13.06	13.16
Cr(III)- <i>p</i> -MCB	Cr(C ₈ H ₇ OS NCl) ₂ Cl.2H ₂ O†	9.89	9.92	12.22	12.24

*N (%): Found, 5.67; calc. 5.75. †N (%): Found, 5.30; calc. 5.30.

TABLE 2 — ELECTRONIC SPECTRAL DATA OF THE COMPLEXES

Complex	$\lambda_{\max}$ (cm ⁻¹)	Δ_0 (cm ⁻¹)	<i>Dq</i> (cm ⁻¹)	<i>B</i> (cm ⁻¹)	β	CFSE (kcal/mole)
Cr(III)-SA	36550* 22730 16390	16390	1639	668.9	0.7265	56.35
Cr(III)-TSA	37798* 16950 13890	16950	1695	691.1	0.7527	58.25
Cr(III)-TGA	38445* 22730 17240	17240	1724	703.65	0.7664	59.27
Cr(III)- <i>m</i> -MAP	38445* 23810 17240	17240	1724	704.0	0.7668	59.27
Cr(III)- <i>p</i> -MCB	39114* 25000 17540	17540	1754	711.8	0.7761	60.29

*Calculated values.

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calculated (Table 2). The Racah parameter (B) and nephelauxetic coefficient (β) are also given in Table 2. These are in good agreement with the data for octahedral Cr(III) complexes reported earlier by us⁴.

The octahedral stereochemistry for the present complexes finds further confirmation from the low values of molar extinction coefficient (~ 25) since the octahedral Cr(III) complexes have ϵ_M values of the order of 10.

The data in Table 2 show that the stability of Cr(III) complexes, based on the 10 Dq values, follows the order: $p\text{-MCB} > m\text{-MAP} > \text{TGA} > \text{TSA} > \text{SA}$ in accordance with the nephelauxetic series.

β -values significantly less than unity indicate $d_{\pi}\text{-}p_{\pi}$ type of interaction between the metal ions and the ligands. This is in agreement with our earlier results¹ obtained from potentiometric studies.

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Nitro & Nitrito Derivatives of Dicyclopentadienyl & Bisindenyl Tungsten(VI) Oxychlorides

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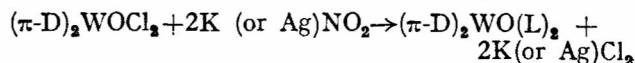
New isomeric nitro and nitrito complexes of tungsten (VI) of general formula $(\pi\text{-D})_2\text{WO(L)}_2$ (where D = cyclopentadienyl or indenyl group and L = nitro or nitrito group) have been prepared. The IR spectra of the complexes indicate that in one case the NO_2 group is linked to the metal via nitrogen whereas in the other via oxygen atom.

DICYCLOPENTADIENYL and bisindenyl tungsten (VI) oxydichlorides are reported in literature¹ and recently we prepared isomeric pseudohalide

derivatives² of the above two compounds. This communication deals with the preparation and characterization of nitro and nitrito derivatives of dicyclopentadienyl and bisindenyl tungsten(VI) oxydichlorides.

All the reactions were carried out in dry atmosphere. All the chemicals used were purified and well dried. Tungsten was estimated as 8-hydroxyquinolate. Presence of cyclopentadienyl, indenyl nitro, and nitrito groups were inferred from IR spectra recorded on a Perkin-Elmer infracord model-137 spectrophotometer in potassium bromide pellets.

Preparation of dicyclopentadienyl oxydinitro tungsten (VI) — Dicyclopentadienyl tungsten(VI) oxydichloride (1 g, 0.0025 mole) was dissolved in tetrahydrofuran (80 ml). Potassium nitrite (0.5 g, 0.006 mole) was added to the solution and the mixture refluxed for 2-3 hr at 65-70°. It was then filtered and the filtrate evaporated to dryness under reduced pressure. The residue after repeated extractions with hot pet. ether (60-80°) gave red-brown crystals of the formula $(\text{C}_5\text{H}_5)_2\text{WO(ONO)}_2$. The nitro derivative was similarly prepared using silver nitrite in place of potassium nitrite and stirring the reaction mixture at room temperature instead of refluxing for 3-4 hr. The bisindenyl tungsten(VI) oxydinitro and dinitrito derivatives were prepared by similar procedures; these compounds were obtained in about 60% yield. The reaction may be represented by the equation:



(where D = cyclopentadienyl or indenyl)

Coordination of NO_2 group via nitrogen to the metal generally raises the asymmetric and symmetric NO_2 frequencies from free ion values^{3,4} (1328 and 1260 cm^{-1}) towards covalently bonded nitro group, e.g. 1586 1377 cm^{-1} respectively in nitromethane⁵. On the other hand, coordination via oxygen raises the asymmetric and lowers the symmetric NO_2 stretching frequencies which for *cis*-methyl nitrite are 1625 and 844 cm^{-1} respectively.⁶ Therefore, the bands assigned to M-NO_2 and M-O-N-O asymmetric and symmetric stretching vibrations (Table 1) are in accord with theoretical expectations^{7,8}. The deformation mode of NO_2 appearing at ~ 820 cm^{-1} does not seem to change very much from the free ion values in either nitro or nitrito derivatives.

TABLE 1 — ANALYTICAL DATA AND SOME CHARACTERISTICS OF NITRO AND NITRITO DERIVATIVES OF DICYCLOPENTADIENYL AND BISINDENYL TUNGSTEN(VI) OXYDICHLORIDES

Compound (colour)	Found (%) (Calc.)				νNO_2 (cm^{-1})	
	W	C	H	N	Asym.	Sym.
$(\pi\text{-C}_5\text{H}_5)_2\text{WO(NO}_2)_2$ (yellow-brown)	43.42 (43.6)	28.61 (28.4)	2.35 (2.37)	6.54 (6.63)	1550	1375
$(\pi\text{-C}_5\text{H}_5)_2\text{WO(ONO)}_2$ (red-brown)	43.51 (43.6)	28.32 (28.4)	2.40 (2.37)	6.56 (6.63)	1585	890
$(\pi\text{-C}_9\text{H}_7)_2\text{WO(NO}_2)_2$ (yellow-brown)	35.12 (35.24)	41.30 (41.38)	2.66 (2.68)	5.40 (5.36)	1550	1380
$(\pi\text{-C}_9\text{H}_7)_2\text{WO(ONO)}_2$ (red-brown)	35.32 (35.24)	41.41 (41.38)	2.71 (2.68)	5.38 (5.36)	1590	880