

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 -MCB $>$ m -MAP $>$ TGA $>$ TSA $>$ SA in accordance with the nephelauxetic series.

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

The authors thank Prof. M. M. Bokadia for facilities and the UGC, New Delhi, for the award of a research grant.

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

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Received 5 June 1975; accepted 28 November 1975

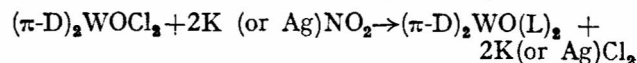
New isomeric nitro and nitrito complexes of tungsten (VI) of general formula $(\pi-D)_2WO(L)_2$ (where D = cyclopentadienyl or indenyl group and L = nitro or nitrito group) have been prepared. The IR spectra of the complexes indicate that in one case the NO_2 group is linked to the metal via nitrogen 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 $(C_5H_5)_2WO(ONO)_2$. 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.)				ν NO_2 (cm^{-1})	
	W	C	H	N	Asym.	Sym.
$(\pi-C_5H_5)_2WO(NO_2)_2$ (yellow-brown)	43.42 (43.6)	28.61 (28.4)	2.35 (2.37)	6.54 (6.63)	1550	1375
$(\pi-C_5H_5)_2WO(ONO)_2$ (red-brown)	43.51 (43.6)	28.32 (28.4)	2.40 (2.37)	6.56 (6.63)	1585	890
$(\pi-C_9H_7)_2WO(NO_2)_2$ (yellow-brown)	35.12 (35.24)	41.30 (41.38)	2.66 (2.68)	5.40 (5.36)	1550	1380
$(\pi-C_9H_7)_2WO(ONO)_2$ (red-brown)	35.32 (35.24)	41.41 (41.38)	2.71 (2.68)	5.38 (5.36)	1590	880

IR spectra, elemental analysis and other properties (Table 1) are in good agreement with the formulae suggested for the derivatives. The IR spectra of these compounds also indicate that the linkage between the cyclopentadienyl and indenyl rings and the metal atom has the character of delocalized π -bonds^{9,10} and the nitro and nitrito groups are attached to the metal by covalent σ -bonds.

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Di-(*p*-chlorophenyl)dithiophosphinato Derivatives of Fe(III), Co(III) & Ru(III)

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Received 5 September 1975; accepted 7 November 1975

Spectral studies in the infrared and visible regions and the magnetic studies over a temperature range (80° to 300°K) of M(III) (M = Fe, Co, Ru) derivatives of di(*p*-chlorophenyl)dithiophosphinic acid (CldtpiH) have been investigated. These complexes have been assigned octahedral stereochemistry and *Dq*, *B* and β values computed wherever possible. A novel mixed complex of Co(III) containing Cldtpi⁻ and dimethylglyoximate anion (Dmg⁻) has been characterized.

THE electron spin resonance, magnetic and spectroscopic studies of dichlorophenyldithiophosphinato (Cldtpi⁻) complexes of some transition metals were reported^{1,2} earlier. The reducing property of this ligand and the stabilization of Co(II) in Co(Cldtpi)₂ which is in contrast to the behaviour of other dithio ligands such as dithiophosphates, dithiocarbamates and xanthates were noted. Therefore, the synthesis of Fe(III) and Co(III) complexes of this ligand are of interest and are reported here together with a novel mixed complex of Co(III) containing Cldtpi⁻ and dimethylglyoximate anion (Dmg⁻). The complex of Ru(III) is included for comparison with iron.

*Fe(Cldtpi)*₃—A concentrated aqueous solution of ferric chloride was neutralized with sodium carbonate and after filtration treated with a slight excess of Na(Cldtpi) in water. The required complex came down as a black precipitate, and was washed with water and dried *in vacuo* (Found S, 18.92; Fe, 5.60. C₃₆H₂₄Cl₆FeP₃S₆ requires S, 19.05; Fe, 5.53%).

The room temperature magnetic moment of 5.85 BM indicated a *d⁵* high spin configuration and the measurements carried over a temperature range of 80° to 300°K indicated the ground state to be ⁶A₁ in an octahedral stereochemistry and no spin equilibrium. The electronic spectrum, which is similar to that of other dithio complexes is dominated by intense charge transfer bands with bands at 16600, 18900 and 23500 cm⁻¹. A slight bathochromic shift of the absorption bands is noticed as the ligand field strength decreases from xanthate to dithiophosphinate. However, no major change in the nature of the spectra is observed between the low spin Fe(ethyl xanthate)₃ to the high spin Fe(Cldtpi)₃.

*Ru(Cldtpi)*₃—Ruthenium trichloride trihydrate (0.5 g) in water (10 ml) was mixed with an aq. solution of Na(Cldtpi) (2 g) and the violet solution so obtained allowed to stand overnight. The deep violet compound which was obtained, was repeatedly washed with water and dried (Found: S, 18.3. C₃₆H₂₄Cl₆P₃RuS₆ requires S, 18.23%).

The complex is stable in air unlike Fe(III) complex and is sparingly soluble in methanol. It is highly soluble in benzene and is monomeric, like other Ru(III) complexes³. The electronic spectrum exhibited bands around 18400, 22300 and 24200 cm⁻¹ (*sh*). The shift of the bands to lower frequency in comparison³ to the spectrum of tris (diethyldithiophosphato)ruthenium(III) [Ru(Et₂dtp)₃], is due to the lower position of dithiophosphinates in the spectrochemical series. The band around 18400 cm⁻¹ have been assigned to the transition⁴ *t_{2g}* → *e_g*. The magnetic moments at 293°K and 83°K were 1.70 and 1.62 BM respectively. The value of 1.70 BM is lower than 2.1 BM expected for a six coordinate Ru(III) complex. This might be due to factors⁵ such as axial distortion, extensive *t_{2g}* electron delocalization, mixing with higher energy components of the ²*I* term or may be due to quenching of the orbital angular momentum by spin orbit coupling which removes the degeneracy of ²*T_{2g}* ground state.

*Co(Cldtpi)*₃—Aqueous solutions of sodium cobaltinitrite and Na(Cldtpi) were mixed together and the required brown complex immediately precipitated. It was washed with water and dried under vacuum (Found: S, 18.72; Co, 5.74. C₃₆H₂₄Cl₆CoP₃S₆ requires S, 18.99; Co, 5.81%).

The complex is quite stable unlike Co(Et₂PS₂)₃ which decomposed even under nitrogen atmosphere⁶. The diamagnetic nature of the compound is indicative of *d⁶* low spin system. The solid state and solution electronic spectra of freshly prepared samples are similar exhibiting bands at 12600 (¹A_{1g} → ¹T_{1g}) and 17900 (¹A_{1g} → ¹T_{1g}). Based on available data⁷, the complex can be assigned an octahedral geometry. The ligand field parameters *Dq*, *B* and β were calculated as 1392 cm⁻¹, 331 cm⁻¹ and 0.32 respectively.

*Co(Cldtpi)*₂(Dmg)—Cobalt chloride hexahydrate dissolved in methanol and a filtered solution of dimethylglyoxime in methanol were mixed together and air was bubbled through the solution for 3 hr. To this a methanolic solution of CldtpiH was added