

# Notes

## Dicarboxylato & Salicylato Chelates of Oxotungsten(VI)

M. K. RASTOGI

Department of Chemistry, Hindu College, Delhi 110007

and

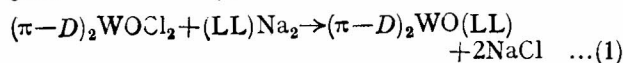
R. K. MULTANI

Department of Chemistry, Delhi University, Delhi 110007

Received 28 September 1976; accepted 3 March 1977

A number of dicarboxylato and salicylato chelates of dicyclopentadienyl-oxotungsten(VI) and bisindenyl-oxotungsten(VI) have been synthesized. Their physical characteristics and IR spectra are reported. The nature of the metal-carboxyl group linkage is discussed.

IN this communication the preparation and characterization of some dicarboxylato and salicylato chelates of dicyclopentadienyl- and bisindenyl-oxotungsten(VI) are reported. The following general reaction (1) was studied:

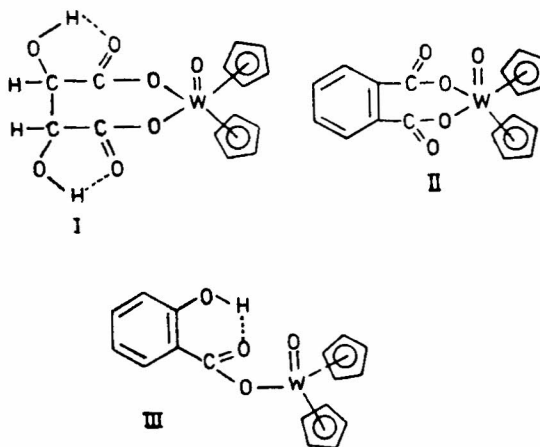


where  $D$  is cyclopentadienyl ( $C_5H_5$ ) or indenyl ( $C_9H_7$ ) group and  $LL$  is the bidentate ligand, namely oxalato, malonato, succinato, tartarato, phthalato and salicylato.

**Preparation of dicyclopentadienyl-oxotungsten(VI) oxalate**  $[(\pi-C_5H_5)_2WO(C_2O_4)]$  — Dicyclopentadienyl tungsten oxydichloride (1.6 g, 0.004 mole) prepared according to published procedure<sup>1</sup> was dissolved in tetrahydrofuran (70 moles). Well-dried potassium oxalate (0.8 g, 0.005 ml) was added to the above solution and the reaction mixture stirred for 3 hr at room temperature and then filtered. The brown-coloured filtrate on evaporation under reduced pressure left a brown residue which was washed with petroleum ether (60-80°) several times. The brown crystalline solid obtained was further recrystallized from tetrahydrofuran. Malonato, succinato, phthalato and salicylato complexes were similarly prepared.

The complexes are brown to dark brown in colour, stable in dry atmosphere except the salicylato derivatives which are sensitive to moisture. They do not sublime or melt but decompose above 150°. They are soluble in common organic solvents but insoluble in water. They are decomposed on heating with dilute acids or alkalis.

The cyclopentadienyl and the indenyl rings are delocalized  $\pi$ -bonded to tungsten and are aromatic in nature as indicated by usual IR bands<sup>2,3</sup>. The aliphatic carboxylato groups showed the usual alkane vibrations<sup>4</sup>, the phthalato and salicylato complexes



showed the bands expected for an *ortho* substituted benzene derivative<sup>5</sup>. Absorption bands  $\sim 1450$  and  $\sim 920$   $cm^{-1}$  indicate a metal to carboxylato linkage<sup>6</sup>, a band  $\sim 1415$   $cm^{-1}$  indicates M-O-C stretching frequency<sup>7</sup> in the salicylato complexes and the band  $\sim 960$   $cm^{-1}$  is due to W=O stretch<sup>8</sup>.

The symmetrical (1275-1390  $cm^{-1}$ ) and the asymmetrical (1675-1700  $cm^{-1}$ )  $\nu O-C-O$  are of interest since their position and separation help in the determination of the nature of bonding between carboxylato group and the metal. The presence of ionic carboxylates is shown by the appearance of  $\nu_{as} O-C-O$  as an intense band in the region 1560-1600  $cm^{-1}$ . In covalently bonded carboxylates there is an increase in the asymmetric and a decrease in the symmetric O-C-O stretches due to the breakdown in equality of the carboxyl groups. Hence a comparison of these two frequencies with the ionic salts on one hand and covalent esters on the other shows that in the present complexes the oxygen to metal bonds have more covalent nature. The increasing order of the degree of covalence may be expressed as: oxalato < malonato, tartarato, salicylato < succinato, phthalato. The shift of carbonyl frequencies in the tartarato complexes may be due to intramolecular hydrogen bonding as shown in structure (I).

This is supported by the appearance of a medium intensity band at 1650  $cm^{-1}$  and a broad but weak band  $\sim 2650$   $cm^{-1}$ , indicating that the second carbonyl is involved in hydrogen bonding or chelation<sup>9</sup>. The lowering of  $\nu O-H$  ( $\sim 3350$   $cm^{-1}$ ) also supports this view. The shift in carbonyl frequencies in phthalato complexes may be due to aryl conjugation<sup>9</sup> as shown in structure (II).

The salicylato complexes are attacked by moisture and the phenolic oxygen to metal bond is disrupted as a broad band of medium intensity appears  $\sim 3500-3400$   $cm^{-1}$  in the IR spectra taken after exposure to moisture. This band may be assigned to  $\nu O-H$ , lowered due to intramolecular hydrogen<sup>9</sup> bonding as shown in structure (III).

## References

- ANAND, S. P., MULTANI, R. K. & JAIN, B. D., *Curr. Sci.*, **17** (1968), 487; *J. organometal. Chem.*, **17** (1969), 423.
- FRITZ, H. P., *Adv. organomet. Chem.*, **1** (1964), 279.
- SCHARF, G. W. & BROWN, R. K., *Can. J. Chem.*, **38** (1960), 697.
- BELLAMY, L. J., *The infrared spectra of complex molecules* (Methuen, London), 1958, 15.
- RAO, C. N. R., *Chemical applications of infrared spectroscopy* (Academic Press, New York), 1963, 201.
- VRATNY, F., RAO, C. N. R. & DILLING, M., *Analyt. Chem.*, **33** (1961), 1455.
- DAVIES, M. & JONES, R. L., *J. chem. Soc.*, (1954), 120.
- KHARITONOV, YU. YA., BURLAEV, YU. A. & KUZNETSOVA, N. A., *Zh. neorg. Khim.*, (1966), 11.
- NAKANISHI, KOJI, *Infrared absorption spectroscopy, Practical* (Nankodo, Japan), 1962, 30.

### Complexes of Co(II), Ni(II), Cu(II), Zn(II) & Cd(II) with Dithiodipropionic Acid

K. C. TEWARI, (Miss) A. VARSHNEY, R. C. GAUR & J. CHANDRA  
Department of Chemistry, Aligarh Muslim University  
Aligarh 202001

Received 20 November 1976; accepted 13 June 1977

Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with dithiodipropionic acid (DTDPA) have been prepared and characterized on the basis of analytical, magnetic moment, conductance, electronic and IR spectral data. The complexes are thermally stable and nonelectrolytic in dimethyl sulphoxide. IR evidence shows that coordination takes place through the sulphur and carboxylate oxygen atoms and the complexes have octahedral structures.

THE chemistry of metal complexes of thiopoly-carboxylic acids<sup>1-6</sup> has been well studied over the past few years. Many metal complexes of ethylene dithiodiacetic acid  $(\text{CH}_2\text{-S-CH}_2\text{-COOH})_2$  have been studied in detail<sup>1,4</sup>. We report here the preparation and characterization of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of isomeric dithiodipropionic acid (DTDPA)  $(\text{S-CH}_2\text{-CH}_2\text{-COOH})_2$ . Dithiodipropionic acid (Evans Chemetics, New York) of 99.5% purity was used without further purification.

For the preparation of complexes, aqueous solution of metal chloride (50 ml, 0.2M) was added to an equimolar solution of DTDPA (150 ml) in ethanol. A few drops of concentrated NaOH were added to adjust the pH of the solution in the range 4-5 and the resulting mixture was then refluxed for 4 hr over a steam-bath. On cooling, a solid separated which was filtered, washed with water and ethanol and dried at 60°.

All the prepared complexes were insoluble in water but slightly soluble in dimethyl sulphoxide and nitrobenzene.

Co(II)-DTDPA complex was a light-pink solid which decomposed at 278° [Found: Co, 19.58; C, 23.82; H, 3.79; S, 21.08.  $\text{Co}(\text{C}_6\text{H}_8\text{S}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$  requires Co, 19.45; C, 23.76; H, 3.98; S, 21.14%].

Ni(II)-DTDPA complex was a green solid which decomposed at 232° [Found: Ni, 17.31; C, 21.34;

H, 4.85; S, 18.72.  $\text{Ni}(\text{C}_6\text{H}_8\text{S}_2\text{O}_4)\cdot 4\text{H}_2\text{O}$  requires Ni, 17.36; C, 21.25; H, 4.75; S, 18.88%]. Thermogravimetric analysis showed loss of two moles of water at 140°.

Cu(II)-DTDPA complex was a bluish-green solid which decomposed at 220° [Found: Cu, 20.74; C, 20.72; H, 3.84; S, 23.28.  $\text{Cu}(\text{C}_6\text{H}_8\text{S}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$  requires Cu, 20.64; C, 20.83; H, 3.92; S, 23.41%].

Zn(II)-DTDPA complex was a white solid which decomposed at 260° [Found: Zn, 23.73; C, 26.30; H, 2.88; S, 23.36.  $\text{Zn}(\text{C}_6\text{H}_8\text{S}_2\text{O}_4)$  requires Zn, 23.89; C, 26.33; H, 2.94; S, 23.43%].

Cd(II)-DTDPA complex was a white solid which decomposed at 237° [Found: Cd, 35.16; C, 22.50; H, 2.66; S, 19.88.  $\text{Cd}(\text{C}_6\text{H}_8\text{S}_2\text{O}_4)$  requires Cd, 35.05; C, 22.48, H, 2.48; S, 19.99%].

The specific conductances of the complexes were determined in saturated solutions of dimethyl sulphoxide using a Philips conductivity bridge model PR-9500. The magnetic measurements were made on a Gouy balance and the diamagnetic corrections applied using Pascal's constants<sup>7</sup>. The electronic (diffusion reflectance) spectra were taken on a Zeiss PMQ II spectrophotometer from the sample diluted with magnesium carbonate and spread on a filter paper. The IR spectra were obtained in nujol on a Perkin-Elmer 621 grating spectrophotometer.

The observed decomposition temperatures (303-304.5°K) and specific conductance values  $(5.0\text{-}6.4 \times 10^{-6})$  in dimethyl sulphoxide, indicate that the complexes are thermally quite stable and nonelectrolytic in nature.

Co(II) complex — The observed magnetic moment of 4.93 BM at 304.5°K is usual and suggests that the complex is octahedral<sup>8</sup>.

The electronic spectrum of the complex shows three hands at 8.3, 17.6 and 20.8 kK which may be interpreted in terms of the transitions  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(v_1)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(v_2)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(v_3)$  respectively in an octahedral field. The ligand field parameters were calculated by the use of semi-empirical equations<sup>9</sup>. The calculated value (0.934) of  $\beta$ , Racah's parameter, relative to the gaseous ion value, indicates a low degree of covalency and the term separation,  $E({}^4P) - E({}^4F)$ , of 13525  $\text{cm}^{-1}$  corresponds to about 94% of the free-ion value<sup>10</sup>. The value of effective spin-orbit coupling constant,  $\lambda$  ( $-153 \text{ cm}^{-1}$ ) as calculated from  $Dq$  and  $B$  values corresponds to 86% of the free-ion value<sup>9</sup> ( $-178 \text{ cm}^{-1}$ ).

Ni(II) complex — The observed magnetic moment value of 3.35 BM at 303.5°K is consistent with the generally accepted values in the range 3.20-3.40 BM for high spin octahedral complexes<sup>6,8,11</sup>. The increase in magnetic moment from the spin-only value could be due to some "mixing in" of upper states via spin-orbit coupling<sup>12</sup>.

The electronic spectrum of the Ni(II) complex shows bands at 8.5, 14.5 and 25.0 kK which may be due to the transitions  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(v_1)$ ,  $\rightarrow {}^3T_{1g}(v_2)$  and  $\rightarrow {}^3T_{1g}(P)(v_3)$  respectively in an octahedral field. These bands are similar to those observed in the case of aquo Ni(II) ion<sup>13</sup>,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ . The ligand field splitting energy,  $10 Dq$ , was taken as