

## Anionic Complexes of Dithiocarboxylates

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WE report preliminary observations on a new series of transition-metal complexes (I) which are formally related to the dithiocarbamates<sup>1</sup> (II) and xanthates<sup>1,2</sup> (III) but possess chemical properties similar to the  $\alpha$ -dithiolates<sup>3-8</sup> (IV).

The simplest member of the series so far is

$M(\text{CS}_3)_2^{2-}$ . Deskin<sup>9</sup> reported the formation constants for the  $\text{Ni}^{\text{II}}$  species but did not isolate the complex. We have prepared the diamagnetic  $\text{Ni}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$ , and  $\text{Pt}^{\text{II}}$  complexes with tetraphenylarsonium cation. The infrared spectra of these 2:1 electrolytes are nearly identical and the  $\text{Ni}^{\text{II}}$

<sup>1</sup> C. M. Harris and S. E. Livingstone in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, ed., Academic Press, New York, 1964, pp. 122-124.

<sup>2</sup> G. W. Watt and B. J. McCormick, *J. Inorg. Nuclear Chem.*, 1965, **27**, 848.

<sup>3</sup> G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 1965, **87**, 3585, and references therein.

<sup>4</sup> A. L. Blach, F. Röhnscheid, and R. H. Holm, *J. Amer. Chem. Soc.*, 1965, **87**, 2301.

<sup>5</sup> J. F. Weiker, L. R. Melby, and R. E. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 4329, and references therein.

<sup>6</sup> H. B. Gray and E. Billig, *J. Amer. Chem. Soc.*, 1963, **85**, 2019.

<sup>7</sup> A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1963, **2**, 1227.

<sup>8</sup> R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *Inorg. Chem.*, 1964, **86**, 113.

<sup>9</sup> W. A. Deskin, *J. Amer. Chem. Soc.*, 1958, **80**, 5680.

and  $\text{Pt}^{\text{II}}$  complexes appear to be isomorphous. The anions are undoubtedly planar.

With X an electron-withdrawing moiety as  $:\text{CHNO}_2$ ,  $:\text{C}(\text{CN})_2$ ,  $:\text{C}(\text{CN})\text{C}_6\text{H}_5$ ,  $:\text{C}(\text{R})\text{NO}_2$ , and  $:\text{NCN}$ , complexes with  $Z = -2$  and  $\text{M} = \text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$ ,  $\text{Pt}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$  have been prepared by treating the appropriate metal ion with the sodium salt of the ligand. While each of the more than thirty-five different complexes represented with the ligands and metals mentioned have not been characterized completely, over half of these have been obtained in a good state of purity.

Some representative properties are reported here for the complexes.

With  $\text{X} = :\text{CHNO}_2$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$ ,  $\text{Pt}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$  complexes with  $Z = -2$  (triphenylbenzylphosphonium cation) have been prepared. The  $\text{Ni}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  complexes are 2:1 electrolytes in nitromethane, ( $10^{-3}\text{M}$ ,  $\Lambda = 155\text{--}165\text{ ohm}^{-1}$  at  $25^\circ\text{C}$ ). Nearly identical infrared spectra are observed with the various metal ions. X-Ray powder patterns of the complexes studied are similar. The platinum complex, and to a lesser extent the others, undergoes reversible chemical oxidation-reduction with iodine and borohydride in 50% v/v dimethylformamide-chloroform. The nickel(II) complex,  $Z = -2$ , is diamagnetic ( $\chi_m = -0.770 \times 10^{-6}$  c.g.s. at ambient temperature). Polarographic oxidations<sup>10</sup> of  $(\text{Et}_4\text{N})_2\text{Ni}(\text{S}_2\text{C}\cdot\text{CH}\cdot\text{NO}_2)_2$  in aqueous solution were found to be pH-dependent, giving two irreversible waves with pH 7 and one irreversible wave with pH 4. In dimethyl sulphoxide containing a small quantity of aqueous acid, with  $0.1\text{N}\text{-Pr}_4\text{NClO}_4$  as the electrolyte, a one-electron reversible wave appears near  $+0.40\text{v}$ . The pH-dependence of the system is reflected in the vivid colour changes which occur on going from acidic to basic solutions. Since protonation can occur at several sites on the complex, it is premature to speculate as to the cause of the pH-dependent properties.

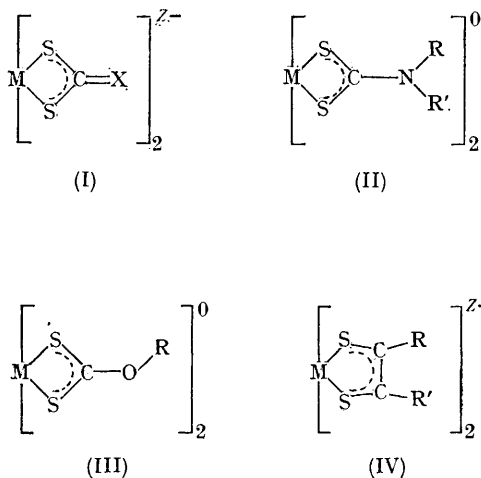
With  $(\text{Pr}_4\text{N})_2\text{Ni}[\text{S}_2\text{CC}(\text{CN})\text{C}_6\text{H}_5]_2$  a reversible

one-electron oxidation wave has been observed in dimethyl sulphoxide at  $+0.122\text{v}$  with a second irreversible wave at  $+0.780\text{v}$ . These oxidations indicate the formation of complexes with  $Z = -1$  and  $Z = 0$ , analogous to the oxidation of the maloneonitrile dithiolate complexes.<sup>4</sup>

With  $\text{X} = \text{C}(\text{CN})_2$ , the  $\text{Pt}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes appear to undergo reversible pH-independent chemical oxidation but polarographically the data are ambiguous.<sup>11</sup> The  $\text{Ni}^{\text{II}}$  complex,  $Z = -2$ , is diamagnetic and with the  $\text{Pr}_4\text{N}^+$  cation is isomorphous with the  $\text{Pt}^{\text{II}}$  complex. The  $\text{Ni}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  complexes are 2:1 electrolytes in nitromethane.

Room temperature e.s.r. signals could not be obtained for any oxidized species.

The infrared spectra and other physical properties of the complexes studied are consistent with four-membered ring structures of the type (I). Where possible, comparisons have been made with the properties of *NN*-dialkyldithiocarbamates which have known<sup>1</sup> chelate structures.



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<sup>10</sup> A rotating platinum electrode with a 1 N-KCl calomel reference electrode was used.

<sup>11</sup> Professor Harry B. Gray (Columbia Univ.) has kindly informed us that several complexes of  $\text{S}_2\text{CC}(\text{CN})_2^{2-}$  have been prepared in his group. The results of these studies will appear in a forthcoming paper in *Inorg. Chem.*