a minimization method which accounts for second order effects are: A_1 = 180 × 10^{-4} cm^{-1}, A_2 = 20 × 10^{-4} cm^{-1}, A_3 = 39 × 10^{-4} cm^{-1}, the A tensor being colinear, within 2°, with the g one.

The ESR data for the complexes show completely anisotropic g values, with the rhombicity, $g_1 - g_2$, increasing on passing from quinoline to water adducts. Further the projection of the g_1 and g_2 directions in the CoO_4 plane are coincident with the projections of the Co–O bond directions in the same plane for (I) while they are rotated by $\simeq$20° for (III). As the structural features of chromophores are quite similar for (I) and (III), the principal cause of these differences must be the different nature of the metal–axial ligand interactions for 6-methylquinoline and water.

The simple assumption of an increase of π-bonding ability, as expected passing from nitrogen bases to water and of the anisotropy of this interaction, based on structural considerations, allowed us to calculate the g and A tensors in a good agreement with the experimental findings. Although the fits we found are not unique, it is important that the experimental data can be reproduced using the minimum number of parameters and varying their values according to the expectations on the chemical behavior of the ligands.

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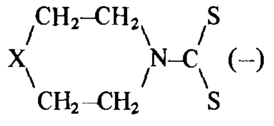
Interactions between Sodium Dithiocarbamates and p- and d-Block Metals

CARLO PRETI*, GIUSEPPE TOSI and PAOLO ZANNINI
Istituto di Chimica Generale ed Inorganica, University of Modena, 41100 Modena, Italy

Working on the problem of the interactions between p- and d-block metals and dithiocarbamate sodium salts as ligands, we report in this study the derivatives of Cr(III), Mn(III), Pb(II), Sn(II), Os(II) and Os(III) with



X	
= CH_2	Pipdtc
= O	Morphdtc
= N–CH_3	CH_3–Pzdtc
= S	Timdtc

We have previously described the complexes of many transition metals with the above dithiocarbamates, derivatives of iridium phosphine and arsine hydrides, and monohalobisdithiocarbamate iron(III), antimony(III) and bismuth(III) derivatives [1].

This paper is an extension of the previously reported studies on the dithiocarbamates in which dialkyl groups are replaced by heterocycles. It is of interest to study the influence of the different heterocyclic groups on the C$\overset{..}{-}$N and C$\overset{..}{-}$S bands and, consequently, on the electronic structure of the complexes. The nature of the heterocycle is important in the behaviour of the dithiocarbamates as ligands owing to the variation in the electron releasing ability of the different amines. The compounds are microcrystalline, soluble in N,N′-dimethylformamide (DMF) and non-conducting in this solvent.

Our manganese(III) derivatives have a μ value in the 4.8–4.9 B.M. range and these values are typical of high-spin complexes. These trisdithiocarbamates can be readily prepared by aerial oxidation of the suspension produced when aqueous or aqueous–ethanolic solutions are mixed. However a recrystallization under nitrogen is necessary to prevent aerial decomposition.

The thioureide band near 1500 cm^{-1} indicates considerable double bond character in C$\overset{..}{-}$N bond. This fact could be ascribed to the electron releasing ability of the heterocyclic group, which forces high electron density towards the sulphur atoms, *via* the π system, thus producing greater double-bond character in the carbon–nitrogen bond, and shifting ν(C$\overset{..}{-}$N) to higher energies. The band attributed to the prevailing contribution of ν(C$\overset{..}{-}$S) is indicative of a bidentate behaviour of the dithioligands and this fact is confirmed by the blue shift of the ν(C$\overset{..}{-}$N) mode.

The ν(C$\overset{..}{-}$N) band undergoes a blue shift greater in the chromium(III), manganese(III), osmium(III) and osmium(II) derivatives than in the tin(II) and lead(II) complexes. This behaviour could be explained by considering either the different stereochemistries of the complexes or the fact that the three first metals are of the d-block, while the last two belong to the p-block. Perhaps because of the rigid heterocyclic ring system, which shows less tendency to release electrons to the carbon–nitrogen bond, this bond has a less double-bond character; this tendency to release electrons is less in the p-block metal derivatives than in the d-block ones.

The electronic spectra have been studied and will be discussed in detail. The room temperature magnetic moment values for Cr(III), Mn(III) and Os(III) derivatives are in agreement with the literature data; all the remaining complexes of Pb(II), Sn(II) and Os(II) are diamagnetic.

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Chemical and Electrochemical Generation of Nickel(III) Poly-aza Macrocyclic Complexes in Aqueous and non-Aqueous Solutions

ANTONIO POGGI and LUIGI FABBRIZZI*

Istituto di Chimica Generale e Inorganica and Laboratorio C.N.R., Università di Firenze, Florence, Italy

It is a property of tetra-aza macrocycles to stabilize unusually high oxidation states of transition metals, which are not accessible to the simple solvocation. A well known example is that of Ni(III), for which extended preparative and electrochemical studies have been reported [1]. We have addressed our attention to the formation of Ni(III) complexes with saturated unsubstituted poly-aza macrocycles of increasing denticity (n = 4, 5, 6) and of varying cavity size. The dark green solutions of the Ni(III) complexes can be prepared through chemical (with $NOBF_4$) or electrochemical (at the platinum anode) oxidation of the corresponding Ni(II) species. The authenticity of the +3 state is demonstrated by the ESR spectra, which are those expected for a low-spin d^7 chromophore in an octahedral environment. The relative solution stability of the Ni(III) species can be expressed by the $E_{1/2}$ value associated to the electrochemically reversible redox change, determined through conventional voltammetric techniques. Most studies have been carried out in acetonitrile, due to the high resistance to the oxidation of this solvent, which allows the attainment also of extremely strong oxidizing species.

For a complete series of 12- to 16-membered tetra-aza macrocycles, the easiest Ni(II)/Ni(III) oxidation process occurs with the symmetric 14-membered system ($E_{1/2}$ = 0.702 V, *vs.* Ag/Ag^+ 0.01 *M*, CH_3CN 0.1 *M* Et_4NBF_4), whereas progressive expansion or contraction of the ligand cavity produces a dramatic increase of the oxidation potential (to 1.12 V). This oxidation selectivity disappears with the introduction of a fifth nitrogen atom in the ligand framework: for a novel series of 15- to 17-membered penta-aza macrocycles, the easiest oxidation occurs with the smallest term ($E_{1/2}$ = 0.732 V), but progressive enlarging of the ligand aperture causes only a moderate increase of $E_{1/2}$ (to 0.817 V). Insertion of a further nitrogen atom, to form the 18-membered cyclic hexamine, makes the attainment of the +3 state somewhat more difficult ($E_{1/2}$ = 0.905 V).

Whereas it is generally believed that the production of Ni(III) polyamine complexes requires strictly anhydrous conditions, relatively stable Ni(III) species can be obtained also in water. Reversible CV profiles are obtained at the carbon paste electrode and the sequence of the $E_{1/2}$ values parallels that found in acetonitrile. However, due to the lower oxidation limit of the water as solvent, only the less oxidizing Ni(III) complexes can be electrochemically or chemically prepared (included that with the open-chain tetramine, 2.3.2-tet).

Reference

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π Interaction in Mixed Ligand Complexes

P. K. BHATTACHARYA* and K. GOPALAKRISHNAN

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda 390 002, India

The study of Cu·dipy·L–L systems, where L–L is a ligand coordinating through two oxygen atoms and has a delocalized π-electron cloud, has shown that $K^{Cu\cdot dipy}_{Cu\cdot dipy\cdot L\text{–}L} > K^{Cu}_{Cu\cdot L\text{–}L}$ [1, 2]. This is because in $Cu(dipy)^{2+}$, Cu(II) has more class 'A' character and hence has greater affinity for the oxygen atoms in the secondary ligand. Further, in case of π-bonding ligands it can be seen that there is a better match between the π-orbitals of Cu·dipy and L–L rather than in Cu·L–L [3]. In other words the π-delocalization between dipyridyl and the secondary ligand is stabilized through the metal ion. The effect is more pronounced in the case of ligands coordinating through oxygen atoms (O–O) because of the additional pair of electrons on the oxygen atoms.

In order to further confirm this fact, the study of the formation constants of complexes of the type Cu·A·L, where A = dipyridyl, *o*-phenanthroline, 2,2′-pyridyl benzimidazoline, 2,2′-pyridyl imidazoline and L = acetoacetanilidide, acetoacet-*o*-anisidide, acetoacet-*o*-toluidide, benzoatoacetanilide have been carried out.

Though the β-ketoanilides have higher K^H values, they form less stable complexes than β-diketones [4]. This shows that π-delocalization is less in metal β