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NEW NITROGEN BASE ADDUCTS OF MANGANESE(II) DIALKYLDITHIOPHOSPHATES AND THE X-RAY STRUCTURE OF $[Mn(phen)_3]^{2+}[S_2P(OC_2H_5)_2^-]_2$

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Abstract—A number of manganese(II) complexes with $[(RO)_2PS_2]^-$ ligands have been prepared and structurally characterized.

A review of the literature[1,2] shows that the chemistry of $Mn^{II}[Rdtp]_2$ ($Rdtp = S_2P(OR)_2^-$) and its adducts with N-bases has been neglected. There are however two papers which refer to $Mn^I[Rdtp(CO)_4]$ ($R = C_6H_5$,[3] CH_3[4]) and their substituted adducts with N-bases and Lewis bases, but these were published over 20 years ago.

Here we report the characterization for a range of complexes of the type $Mn[Rdtp]_2 \cdot L$, [$R = C_2H_5$, *i*-C_3H_7, *n*-C_4H_9; L = bipy (2,2′-bipyridyl), phen (1,10-phenanthroline), dmphen (2,9-dimethyl,1,10-phenanthroline)] and $[Mn(phen)_3]^{2+}$ $[Rdtp^-]_2$ ($R = C_2H_5$, *i*-C_3H_7). It is surprising that although the $[Mn(phen)_3]^{2+}$ cation has long been known to possess anti-fungal[5] and more recently anti-venereal and contraceptive properties,[6] its single crystal X-ray structure has not been reported,[2] and so we have carried out such a study on $[Mn(phen)_3]^{2+}[Rdtp^-]_2$ ($R = C_2H_5$), and this is described below.

The $Mn[Rdtp]_2 \cdot L$ complexes were prepared by mixing solutions of $[NH_4][Rdtp]$ in H_2O and the appropriate N-base in ethyl alcohol with aqueous $Mn(NO_3)_2 \cdot 6H_2O$ in a stoichiometric ratio. All the complexes described here have been characterized by elemental analysis and IR spectra. Yields are generally in excess of 60%.

The nature of the products [shown in eqs (1)–(3)] is dependent upon L, substituent R and the solvent. When the ratio of metal salt–Rdtp–phen is 1 : 2 : 1, then $Mn(Rdtp)_2 \cdot L$ is precipitated in H_2O for $R = C_2H_5$ and *n*-C_4H_9, but not when R = *i*-C_3H_7. On increasing the relative ratio of phen from 1 to 3, no change in product was observed. When L = bipy, only when R = *n*-C_4H_9 is the compound $Mn[Rdtp]_2 \cdot L$ formed. But on extraction with CH_2Cl_2 from a mixture of solutions of Mn^{II}, $Rdtp^-$ and L in the ratio 1 : 2 : 1, a larger range of complexes of this type are obtaind ($R = C_2H_5$, *i*-C_3H_7; L = phen, bipy, dmphen; and R = *n*-C_4H_9, L = dmphen). In the case of $R = C_2H_5$, L = phen, the major product was yellow crystals of $Mn[Rdtp]_2(phen)$. However, small traces of red crystals were also observed, which were separated by repeated recrystallization and characterized as $[Mn(phen)_3]^{2+}[Rdtp^-]_2$.

On the other hand, treatment of $Mn(Rdtp)_2 \cdot L$ ($R = C_2H_5$; L = phen) with 2 mol equivalent of phen gave a yellow complex in quantitative yield, which was identified as $[Mn(phen)_3]^{2+}[Rdtp^-]_2$. This is in marked contrast to the reaction with bipy, where $Mn(Rdtp)_2 \cdot L$ undergoes oxidation to give MnO_2, the disulphide[7] $[(RO)_2P(S)S^-]_2$ (^{31}P NMR, 83.7 ppm) and bipy. Holah and Murphy isolated $[Mn(phen)_3]^{2+}$ with a similar ligand, e.g. $S_2COC_2H_5^-$, by mixing Mn^{II}, $S_2COC_2H_5^-$, and phen (1 : 2 : 3) in water, but found that with bipy,

$$Mn^{II} + 2Rdtp^- + L \xrightarrow[H_2O]{} Mn[Rdtp]_2 \cdot L \qquad (1)$$

$$Mn[Rdtp]_2 \cdot L + 2L \xrightarrow[C_2H_5OH]{} \begin{cases} [MnL_3]^{2+}[Rdtp^-]_2 \quad (R = C_2H_5,\ L = \text{phen})\ 90\%\ \text{yield} & (2) \\ MnO_2 + L + \{(RO)_2P(S)S^-\}_2 \quad (R = C_2H_5,\ L = \text{bipy}) & (3) \end{cases}$$

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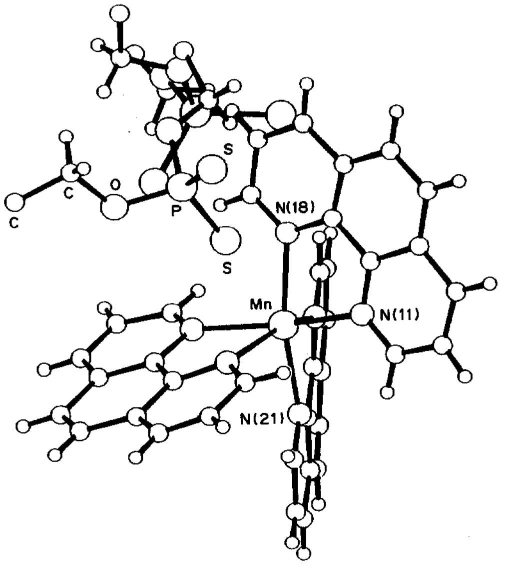

Fig. 1

intractable oils were obtained which could not be characterized.[8]

The above results are not unexpected since complexes of phen with other transition metals are generally more stable[9] than with bipy.

A crystal structure determination was carried out on the yellow crystals of $[Mn(phen)_3]^{2+}[Rdtp^-]_2$ ($R = C_2H_5$).* Preliminary investigations show that the red crystals isolated from the preparation of $Mn[dtp]_2(phen)$ are isomorphous, so we have no immediate explanation for the variation in the colour. Spectral measurements on the two compounds are similar.

The structure is shown in Fig. 1; there are only van der Waals contacts between the ions. In the cation the independent Mn—N distances are 2.224(18), 2.285(13) and 2.263(12) Å. The geometry of the metal atom coordination sphere can be described as distorted octahedral. The main features of the distortion arise from the N—Mn—N chelate angle, for which the mean value is 73.4°. It is noteworthy that of the three *trans* N—Mn—N angles, one at 153.4(5)°, is significantly shorter than the other two [163.6(5)°]. Dimensions in the $Rdtp^-$ anion are compatible with previous studies.[7] Further X-ray and spectroscopic studies on compounds in this series are in progress.

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* Crystal data: $[Mn(phen)_3]^{2+}[Rdtp^-]_2$ (**1**), $C_{44}H_{44}N_6S_4O_4P_2Mn$, $M = 965.47$, monoclinic, $a = 16.55(1)$, $b = 17.50(1)$, $c = 17.46(1)$, $\beta = 93.0(1)$, $U = 4680.0$ Å^3, $F(000) = 2004$, $d_m = 1.37(2)$ g cm^{-3}, $d_c = 1.37$ g cm^{-3}, $Z = 4$, $F(000) = 506$, Mo-K_α radiation, $I = 0.7107$ Å, $\mu = 5.85$ cm^{-1}, space group $I2/c$ (No. 15). The structure was determined by statistical methods. The structure consists of $[Mn(phen)_3]^{2+}$ cations with crystallographically imposed C_2 symmetry and discrete $dedtp^-$ anions in general positions. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, although the methyl hydrogen atoms were refined as rigid groups. The final R was 0.098 ($R_w = 0.097$) for 1565 independent data with $I > 2\sigma(I)$. Atomic coordinates, displacement factor coefficients, full lists of bond lengths and angles have been deposited as supplementary data with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.