

A MANGANESE(III) HETEROCHELATE:
BIS(BIGUANIDO)(BENZOYLACETONATO)MANGANESE(III)*

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In previous communications^{1,2} we have reported several new coordination complexes of manganese(III) including the first heterochelate, hydroxo-aquo(biguanido)-(acetylacetonato)manganese(III). In the course of our attempts to synthesize new coordination complexes of manganese(III), we have now isolated and characterized what is believed to be the second heterochelate in this series. This report is concerned with the preparation and magnetic and spectral properties of bis(biguanido)(benzoyl-acetonato)manganese(III). This has been obtained as orange-brown microcrystals by the interaction of Mn bzac₃ (bzac = benzoylacetone minus one proton) and free biguanide in 1 : 2 mole ratio in dry ethanol. The published preparative method for Mn bzac₃ was not available. The procedure for the analogous acetylacetone complex³ was adapted and the purity of the product was checked by analysis.

The effective magnetic moment (μ_{eff} 4.58 B.M.) is fairly close to the spin-only value for four unpaired electrons and is indicative of a spin-free manganese(III) complex. The 3+ oxidation state of the manganese in the complex was confirmed by iodometric titration. The compound liberated 1 equiv. of iodine per manganese atom. Though the molar conductivity of the compound is far below the value for a 1 : 1 electrolyte, it is at variance with its formulation as non-electrolyte. As suggested earlier,¹ the slight conductance in methanol and feeble alkalinity might be due to protonation of the coordinated biguanide by water in the solvent. However, from a consideration of the preparative medium for the heterochelates, it appears that some slight contamination with basic impurities is not unlikely. This can as well be responsible for the observed conductance, without seriously affecting the elementary analyses.

The spectra of six-coordinated high-spin manganese(III) complexes have been interpreted⁴ in terms of O_h symmetry and the 20000 cm⁻¹ band (ϵ 50–300 l. mole⁻¹ cm⁻¹) assigned to the spin-allowed crystals field transition, ${}^5E_g \rightarrow {}^5T_{2g}$. The visible spectrum of Mn bzac₃ in CCl₄ shows this band at 17900 sh cm⁻¹. The spectrum of the heterochelate, measured in the region 17800–2700 cm⁻¹, consists of intense bands at 25200 cm⁻¹ ($\log \epsilon$ 3.60) and 22990 sh cm⁻¹ ($\log \epsilon$ 3.51). Similar overlapping bands with large extinction coefficients (25600 cm⁻¹, $\log \epsilon$ 3.4, and 23200 cm⁻¹, $\log \epsilon$ 3.2) have been observed in the spectrum of the heterochelate reported previously.¹ These were

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¹ Ray, M. M., Adhya, J. N., Biswas, D. K., and Poddar, S. N., *Aust. J. Chem.*, 1966, **19**, 881.

² Ray, M. M., Adhya, J. N., Biswas, D. K., and Poddar, S. N., *Aust. J. Chem.*, 1966, **19**, 1737.

³ Fernelius, W. C., and Bryant, B. E., *Inorg. Synth.*, 1957, **6**, 105.

⁴ Dingle, R., *Acta chem. scand.*, 1966, **20**, 33.

tentatively assigned as the split components of the ${}^5E_g \rightarrow {}^5T_{2g}$ transition. Both the splitting, and the intensity which is unusually high for a $d-d$ transition, were attributed to the asymmetric ligand field. It was, however, suggested that the higher energy band might have originated in one of the several possible electron-transfer transitions.⁵ It is quite probable that the disparate intensity of both the bands in the near u.v. spectra of the heterochelates is due to electron transfer which totally obscures the close-by $d-d$ transition.

Experimental

Tris(benzoylacetonato)manganese(III)

A solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (2.5 g) in 1:1 water-ethanol (30 ml) was mixed with a solution of benzoylacetone (16 g) in ethanol (20 ml). The mixture was briefly heated on a steam-bath, and a solution of KMnO_4 (0.5 g) in water (20 ml) was added slowly with stirring when a greenish yellow colour developed. Sodium acetate (6.2 g) dissolved in ethanol (20 ml) was then added and the mixture warmed on a steam-bath; a gummy material was deposited. The liquid was decanted off. The gummy mass solidified on being digested with cold water. This was collected and dissolved in hot acetone. On evaporation the acetone solution yielded greenish black shining crystals (Found: Mn, 10.3. Calc. for $\text{C}_{39}\text{H}_{27}\text{MnO}_6$: Mn, 10.2%).

Bis(biguanido)(benzoylacetonato)manganese(III)

Biguanide normal sulphate (1.5 g, 0.005 mole equiv. to 0.01 mole of biguanide) was added to a solution of metallic sodium (0.23 g, 0.01 g-atom) in dry ethanol (20 ml). The mixture was refluxed on a steam-bath for 2 hr. The precipitated sodium sulphate was filtered off. The filtrate containing free biguanide was mixed with Mn bzac_3 (1.3 g, 0.005 mole) and the mixture refluxed for 2 hr, whereupon the colour changed to red. The solution was concentrated in vacuum over fused calcium chloride, and then dry ether was added. The orange-brown microcrystals that separated were filtered, washed successively with dry ether, and kept in vacuum (Found: Mn, 12.95; N, 33.7. Calc. for $\text{C}_{14}\text{H}_{21}\text{MnN}_{10}\text{O}_2$: Mn, 13.3; N, 33.8%).

In a typical oxidimetric titration¹ 0.02695 g of the sample consumed 3.7 ml of thiosulphate (0.01852N) (calc. 3.49 ml). The heterochelate is soluble in water, but is rapidly hydrolysed on standing; it is soluble in methanol giving a stable solution.

The conductivity of the heterochelate ($7.243 \times 10^{-4}\text{M}$ in methanol) and its magnetic data (at 26.5°) are as follows: λ $40.4 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$; χ_g 19.55×10^{-6} CGS units; μ_{eff} 4.58 B.M.

The spectrum was measured in methanol with a Hilger Uvispek spectrophotometer. The conductivity was measured with a Mullard conductivity bridge. The magnetic measurement was made with a Curie balance.

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⁵ Jørgensen, C. K., *Acta chem. scand.*, 1962, **16**, 2406.