

Seven-co-ordinate Complexes of Iron(III)

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WE report here seven-co-ordination in several iron(III) complexes of a pentadentate macrocyclic ligand, 2,13-dimethyl-3,6,9,12,18-penta-azabicyclo-[12,3,1]octadeca-1(18),2,12,14,16-pentaene [structure (I)].

The new compounds are crystalline solids of the stoichiometry FeBX_2Y , where B = macrocyclic ligand, X = Cl, Br, I, or NCS, and Y = ClO_4 , BF_4 , or NCS, that are moderately soluble in water and in polar organic solvents. The colours of the crystals vary with the group X: Cl, yellow; Br, orange; I, dark green; NCS, deep red (large crystals appear green). Infrared spectra show the ligand to be that reported earlier¹ in $\text{FeB(OH)(ClO}_4)_2$, a substance having a room-temperature magnetic moment of 1.9 B.M. The magnetic moments of the new compounds FeBX_2Y are close to the value of 5.92 B.M. predicted for high-spin iron(III).

For the six salts $[\text{FeBCl}_2]\text{ClO}_4$, $[\text{FeBCl}_2]\text{BF}_4$, $[\text{FeBBr}_2]\text{ClO}_4$, $[\text{FeBI}_2]\text{ClO}_4$, $[\text{FeB(NCS)}_2]\text{ClO}_4$, and $[\text{FeB(NCS)}_2]\text{NCS}$, the molar conductances fall within the range expected for uni-univalent electrolytes in nitromethane.²

The absorption pattern in that portion of the infrared spectrum near 1100 cm^{-1} indicates that the ClO_4^- and BF_4^- are not co-ordinated.³ Also, for $[\text{FeB(NCS)}_2]\text{ClO}_4$ the antisymmetric stretch of NCS falls at 2040 cm^{-1} , whereas in $[\text{FeB(NCS)}_2]\text{NCS}$ a second weaker band is observed at 2055 cm^{-1} , in addition to the 2040 cm^{-1} absorption, indicating that two of the three NCS groups are co-ordinated in the latter. Co-ordination of the anions is evidenced independently by a strong absorption band in the visible or ultraviolet spectra of nitromethane or methanol solutions of these compounds.

The high molar-extinction coefficients ($\epsilon_{\text{M}} = 5600\text{--}15,500$) suggest that the absorption involves a charge-transfer transition. The position of λ_{max} varies as expected for the halide complexes (Cl, 362; Br, 442; I, 630 $\text{m}\mu$). The spectra of the several salts in water, where they are fully ionized, are identical.

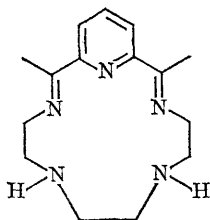
We have assumed that all five of the nitrogen atoms of B are co-ordinated. If one were free, it should be readily protonated. Attempts to isolate a protonated derivative failed. Indeed, the compounds were most often prepared by treatment of acidified solutions of the previously reported complex $\text{FeB(OH)(ClO}_4)_2$ with NaX.

The earlier report that the magnetic moment of the parent compound $\text{FeB(OH)(ClO}_4)_2$ corresponds to that expected for low-spin d^5 in a ligand field of low symmetry does not accommodate to the structural model given above, for there is no reason why it should be low-spin when all other $[\text{FeBX}_2]^+$ are high-spin. Obviously a dimeric structure with spin-spin exchange could account for this behaviour.⁴ This has been confirmed by study of the temperature-dependence of the magnetic susceptibility, which shows a maximum at 270° K .

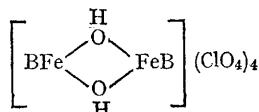
The most likely seven-co-ordinate structures for the dimer involve double hydroxo-bridges between metal atoms [structure (II)] or a single oxo-bridge [structure (III)] with co-ordination of additional anions and/or solvent. The evidence at hand favours structure (III). (a) Strong broad infrared absorption occurring at 795 cm^{-1} , only in the bridged complex, is unaffected by deuteration or loss of H_2O , and may be attributed to M-O-M (M = metal) stretching vibrations.⁵ (b) The molar

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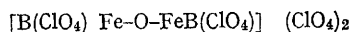
conductance for the dimer in 10^{-3} M-nitromethane solutions is $164 \text{ ohm}^{-1} \text{ cm.}^{-1}$, a value consistent with structure (III), but not structure (II). (c) The breadth and profile in the region $900\text{--}1200 \text{ cm.}^{-1}$ in the infrared spectrum is best interpreted in terms



(I)



(II)



(III)

of overlapping modes due to both co-ordinated and ionic ClO_4 groups.³ The infrared spectrum of the derivative $[\text{B}(\text{NCS})\text{Fe-O-FeB}(\text{NCS})](\text{ClO}_4)_2$ suggests the presence of only ionic ClO_4 .

The occurrence of the co-ordination numbers of seven among these compounds is traceable to the conformational constraints, for the pentadentate ligand is not well suited to co-ordinate on an octahedron. If all five donor atoms of the macrocycle are coplanar, the anions would occupy sites above and below the plane in a distorted pentagonal bipyramidal structure; however, the least strain (Dryden stereomodels) is found when the ligand is folded so that the donor atoms of the macrocycle define two planes. In the case of extreme folding, the anions are expected to occupy mutually *cis*-positions on a single side of the ring. An intermediate structure is anticipated in which the anions are *trans* (on opposite sides of the macrocycle), but the ligand is not expected to maintain its donor atoms in a strictly planar array.

(Received, July 11th, 1966; Com. 482.)

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⁴ J. Lewis, F. Mabbs, and A. Richards, *Nature*, 1965, **207**, 855.

⁵ (a) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3552; (b) A. Earnshaw and J. Lewis, *ibid.*, 1961, 396.