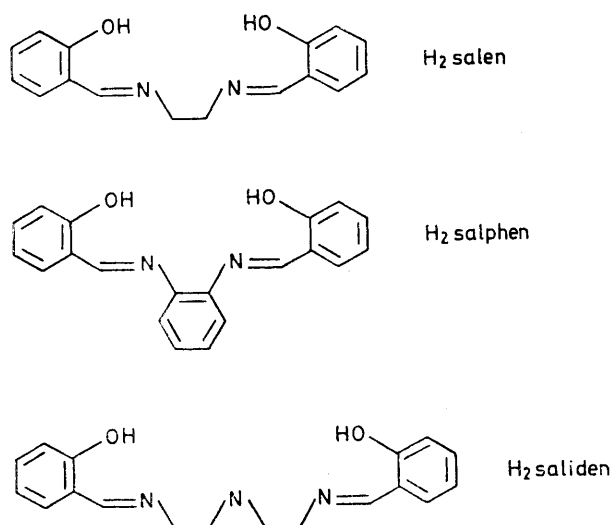


Mixed Iron(III) and Molybdenum(VI) Complexes with Schiff Bases

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Schiff-base complexes, $[(\text{FeL})_2\text{Mo}_a\text{X}_b]$, have been prepared [$\text{H}_2\text{L} = \text{NN}'$ -ethylenebis(salicylideneimine), $\text{X} = \text{O}$, $a = b = 1$, $\text{X} = \text{S}$, $a = 2$, $b = 7$; $\text{H}_2\text{L} = \text{NN}'$ -*o*-phenylenebis(salicylideneimine), $\text{X} = \text{O}$, $a = 2$, $b = 7$; $\text{H}_2\text{L} = 3,3'$ -iminodiethylenebis(salicylideneimine), $\text{X} = \text{O}$, $a = b = 1$]. Magnetic properties and spectra (i.r., u.v., visible, and Mössbauer) are reported. The complexes are binuclear with bridging molybdate or thiomolybdate anions, but the spin coupling between iron atoms is much less than in the analogous oxo- and thio-bridged complexes.

REACTIONS of oxo- and thio-molybdates(VI) with complexes of iron(III) are relevant to the co-ordination chemistry of molybdate anions and, possibly, to iron-molybdenum relations in biological systems.¹⁻⁵ Molybdate(VI) forms a complex with iron(III) protoporphyrin IX (haemin), and haemin catalyses the oxidation by molybdate(VI) of $[\text{S}_2\text{O}_3]^{2-}$, Fe^{2+} , Cu^+ , and I^- .⁵ In this paper we describe the preparation of Schiff-base complexes containing both molybdenum and iron and show that molybdate and thiomolybdate can replace oxide as bridging ligands in bi- and poly-nuclear iron(III) complexes. The structure of the Schiff bases are given below.



EXPERIMENTAL

Preparations and Analyses.— μ -Oxo-bis{[NN'-ethylenebis(salicylideneiminato)]iron(III)}, $[\{\text{Fe}(\text{salen})\}_2\text{O}]$. Stoichiometric amounts of salicylaldehyde and ethylenediamine

were added to an aqueous solution of iron(II) sulphate.⁶ The crude product was recrystallised three times from pyridine-ethanol and dried *in vacuo* (Found: C, 58.2; H, 4.3; Fe, 16.9; N, 8.5. Calc. for $\text{C}_{32}\text{H}_{28}\text{Fe}_2\text{N}_4\text{O}_5$: C, 58.2; H, 4.3; Fe, 16.9; N, 8.5%).

μ -Tetraoxomolybdate(VI)-bis{[NN'-ethylenebis(salicylideneiminato)]iron(III)}, $[\{\text{Fe}(\text{salen})\}_2\text{MoO}_4]$. (a) A solution of sodium molybdate dihydrate (0.6 g) in water (8 cm³) was added to a solution of the complex $[\{\text{Fe}(\text{salen})\}_2\text{O}]$ (2.1 g) in a mixture of water (150 cm³), methanol (150 cm³), and salicylaldehyde (3 cm³). The resulting solution was left for ca. 15 h. A precipitate which had formed was filtered off, washed with water, and boiling chloroform, and dried *in vacuo* over P_4O_{10} (Found: C, 47.9; H, 3.5; Fe, 14.0; Mo, 12.1; N, 6.9. $\text{C}_{32}\text{H}_{28}\text{Fe}_2\text{MoN}_4\text{O}_8$ requires C, 47.9; H, 3.5; Fe, 13.9; Mo, 12.0; N, 7.0%).

(b) Salicylaldehyde (4.2 cm³) and ethylenediamine (1.25 cm³) were added to a solution of iron(II) sulphate hexahydrate (5.6 g) in water (150 cm³) and methanol (150 cm³). The mixture was heated on a water-bath and a precipitate of $[\{\text{Fe}(\text{salen})\}_2\text{O}]$ formed. The precipitate was filtered off and a solution of $\text{Na}_2[\text{MoO}_4] \cdot 2\text{H}_2\text{O}$ (0.6 g) in water (8 cm³) was added to the filtrate. The mixture was heated on a water-bath and the brown precipitate which formed was filtered off and dissolved in boiling methanol. The methanol solution was filtered and the brown solid was reprecipitated by addition of water. The product was filtered off, washed with cold methanol, and dried *in vacuo* over P_4O_{10} (Found: C, 47.9; H, 3.5; Fe, 13.9; Mo, 12.0; N, 7.0. $\text{C}_{32}\text{H}_{28}\text{Fe}_2\text{MoN}_4\text{O}_8$ requires C, 47.9; H, 3.5; Fe, 13.9; Mo, 12.0; N, 7.0%).

μ -Heptathiodimolybdate(VI)-bis{[NN'-ethylenebis(salicylideneiminato)]iron(III)}, $[\{\text{Fe}(\text{salen})\}_2\text{Mo}_7\text{S}_7]$. Salicylaldehyde (4.2 cm³) and ethylenediamine (1.25 cm³) were added to a solution of $\text{Fe}[\text{SO}_4] \cdot 6\text{H}_2\text{O}$ (5.6 g) in a mixture of water (150 cm³) and methanol (150 cm³). The mixture was warmed on a water-bath, cooled, and a precipitate of $[\{\text{Fe}(\text{salen})\}_2\text{O}]$ was filtered off. An excess of a freshly

* S. Green and A. Mazur, *J. Biol. Chem.*, 1957, **227**, 653; A. Mazur, S. Green, A. Saha, and A. Carleton, *J. Clin. Investigation*, 1958, **37**, 1809.

* S. B. Brown, P. Jones, K. Prudhoe, and A. Suggett, *Nature*, 1968, **219**, 605.

* P. Pfeiffer, E. Breith, E. Lübke, and T. Tsumaki, *Ann. Chim.*, 1933, **503**, 84.

¹ J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475.

² M. S. Seelig, *Amer. J. Clin. Nutrition*, 1972, **25**, 1022; 1973, **26**, 757.

³ Th. G. Spiro and P. Saltman, *Structure and Bonding*, 1969, **6**, 116.

prepared solution of ammonium tetrathiomolybdate (2.0 g) in water (30 cm³) was added to the filtrate. A brown solid formed, and was filtered off, washed with water, and dried *in vacuo* over P₄O₁₀ (Found: C, 36.0; H, 2.7; Fe, 10.3; Mo, 18.0; N, 5.2; S, 20.9. C₃₂H₂₈Fe₂Mo₂N₄O₄S₇ requires C, 36.2; H, 2.6; Fe, 10.5; Mo, 18.1; N, 5.3; S, 21.1%).

μ -Oxo-bis{[NN'-o-phenylenebis(salicylideneiminato)]iron(III)}, [{Fe(salphen)}₂O]. Stoichiometric amounts of salicylaldehyde and o-phenylenediamine were added to an aqueous solution of Fe[SO₄]. The crude product was recrystallised from dichloromethane and dried at ca. 80 °C *in vacuo* (Found: C, 63.3; H, 3.6; N, 7.5. Calc. for C₄₀H₂₈Fe₂N₄O₅: C, 63.5; H, 3.7; N, 7.4%).

Attempted preparation of an iron-molybdenum(vi) complex of NN'-o-phenylenebis(salicylideneimine), H₂salphen. Salicylaldehyde (4.2 cm³) and o-phenylenediamine (2.2 g) in methanol (30 cm³) were added to a solution of hydrated Fe[SO₄].6H₂O (5.6 g) in a mixture of water (150 cm³) and methanol (150 cm³). The mixture was heated and stirred on a water-bath, cooled, and the oxo-bridged complex was filtered off. A solution of Na₂[MoO₄].2H₂O (0.6 g) in water (8 cm³) was added to the filtrate. There was an immediate light brown precipitate which was filtered off, and washed with water and methanol (Found: C, 50.5; H, 3.0; Fe, 4.6; Mo, 19.4; N, 5.8. C₁₀₀H₇₀Fe₂Mo₅N₁₀ requires C, 50.6; H, 3.0; Fe, 4.7; Mo, 20.2; N, 5.9%).

μ -Tetraoxomolybdate(vi)-bis{[3,3'-iminodiethylenbis(salicylideneiminato)]iron(III)}, [{Fe(saliden)}₂MoO₄]. Salicylaldehyde (4.2 cm³) and 3-azapentane-1,5-diamine (3 cm³) were added to a solution of hydrated Fe[SO₄].6H₂O (5.6 g) in a mixture of water (150 cm³) and methanol (150 cm³). The solution was evaporated in a rotary evaporator and a dark red oily solid was obtained. Analyses of this product were variable on repeated preparations and attempted recrystallisation was unsuccessful. The red solid was dissolved in a mixture of ethanol (200 cm³) and water (100 cm³) and the solution was filtered. A solution of Na₂[MoO₄].2H₂O (1.0 g) in water (20 cm³) was added to the filtrate and a red crystalline product was formed. The product was filtered off, washed with ethanol, and dried *in vacuo* over P₄O₁₀ (Found: C, 48.7; H, 4.3; Fe, 12.6; Mo, 10.7; N, 9.3. C₃₆H₃₈Fe₂MoN₆O₈ requires C, 48.6; H, 4.3; Fe, 12.5; Mo, 10.8; N, 9.3%).

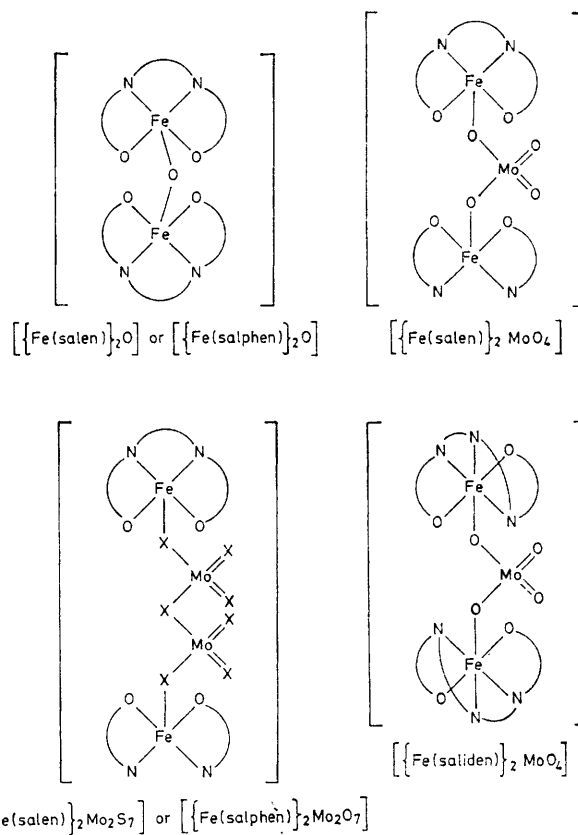
Physical Measurements.—U.v. and visible spectra were recorded for solutions, and for solids by diffuse reflectance against magnesium oxide, on a Unicam SP 700 spectrophotometer. I.r. spectra (KBr discs and Nujol mulls) were obtained on a Unicam SP 200 spectrophotometer. Magnetic susceptibilities were measured on a Newport Instruments Ltd. variable-temperature Gouy balance system. Mössbauer spectra were recorded at 300 K by the Physicochemical Measurements Unit, Harwell, using a ⁵⁷Co source and a standard iron calibrant.

Analyses.—The complexes were decomposed by fusion with sodium carbonate. Molybdenum was determined gravimetrically as the quinolin-8-olate complex, [MoO₂-(quin)₂], and iron by cerium(IV) titration after reduction with zinc amalgam. Carbon, hydrogen, and nitrogen were determined by standard microanalytical methods.

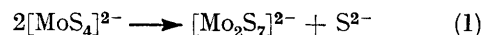
RESULTS AND DISCUSSION

Reactions Studied and Complexes Prepared.—We have prepared complexes of Schiff bases containing both iron and molybdenum. On the basis of our physical measure-

ments (see below) the molybdenum-containing complexes are analogous to the well known oxo-bridged iron(III) Schiff-base complexes,⁷ with molybdate or thiomolybdate in place of oxide. Structures are shown below.



The molybdate-bridged complexes were obtained by adding molybdate to methanol-water solutions of the corresponding oxo-bridged complexes or to the filtrates remaining after isolation of the oxo-bridged complexes. We were unable to obtain pure samples of a molybdate-bridged complex corresponding to the complex $\left[\left\{ \text{Fe(salphen)} \right\}_2 \text{O} \right]$. The products, according to analyses and physical measurements, were mixtures of the complexes $\left[\left\{ \text{Fe(salphen)} \right\}_2 \text{Mo}_2 \text{O}_7 \right]$ and $\left[\text{MoO}_2(\text{salphen}) \right]$. The thiomolybdate complex $\left[\left\{ \text{Fe(salen)} \right\}_2 \text{Mo}_2 \text{S}_7 \right]$ was prepared by adding $\left[\text{NH}_4 \right]_2 \left[\text{MoS}_4 \right]$ to the filtrate from the isolation of the oxo-complex $\left[\left\{ \text{Fe(salen)} \right\}_2 \text{O} \right]$. At the pH of the filtrate (ca. 5), the $\left[\text{MoS}_4 \right]^{2-}$ ion dimerises [equation (1)].⁸



A slight excess of thiomolybdate was needed to obtain the complex $\left[\left\{ \text{Fe(salen)} \right\}_2 \text{Mo}_2 \text{S}_7 \right]$; with less thiomolybdate the product was contaminated with the thio-bridged complex $\left[\left\{ \text{Fe(salen)} \right\}_2 \text{S} \right]$.⁹ Our preparative work sug-

⁷ K. S. Murray, *Co-ordination Chem. Rev.*, 1974, **12**, 1.

⁸ R. Saxena, M. Jain, and M. Mittol, *Austral. J. Chem.*, 1968, **21**, 91.

⁹ P. C. H. Mitchell and D. A. Parker, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1385.

gests that in solution the binuclear complexes $[(\text{FeL})_2\text{O}]$ (H_2L = Schiff base) are in equilibrium with mononuclear complexes $[\text{FeL}]^+$ {or $[\text{FeL}(\text{OH}_2)]^+$ } which may combine with anions such as molybdate also in the solution giving aniono-bridged complexes which are less soluble than the oxo-bridged complexes.

I.r. Spectra.—The Schiff-base complexes have a strong band at *ca.* 1540–1545 cm^{-1} which is assigned to the C=N stretching vibration and shows that the Schiff bases are co-ordinated.¹⁰ Of particular interest is the 700–1000 cm^{-1} region where characteristic MoO¹¹ and FeO vibrations occur.⁹ Spectra in this region, and

vibrations at 950, 910, 860, and 800 cm^{-1} . Since there were no OH vibrations, all the Schiff bases must be co-ordinated; only two can be accounted for by co-ordination to the iron, and the remaining three must therefore be co-ordinated to molybdenum. We suggest that the 'complex' is a 1:3 mixture of $[\{\text{Fe}(\text{salphen})\}_2\text{Mo}_2\text{O}_7]$ and $[\text{MoO}_2(\text{salphen})]$. The high-wavenumber band (950 cm^{-1}) could then be accounted for by terminal oxide in the Mo_2O_7 bridge (see below) or the MoO_2 group.¹¹

For the oxo-bridged complexes $[\{\text{Fe}(\text{salen})\}_2\text{O}]$ and $[\{\text{Fe}(\text{salphen})\}_2\text{O}]$ there is a strong band at 830 cm^{-1} which is not observed for the molybdato- or thio-bridged

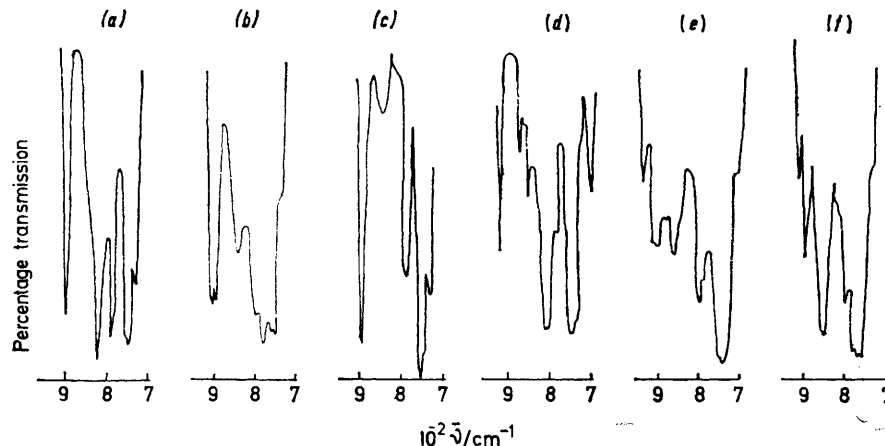


FIGURE 1 I.r. spectra (KBr discs) in the region of Mo-O stretching vibrations for (a) $[\{\text{Fe}(\text{salen})\}_2\text{O}]$, (b) $[\{\text{Fe}(\text{salen})\}_2\text{MoO}_4]$, (c) $[\{\text{Fe}(\text{salen})\}_2\text{S}]$ and $[\{\text{Fe}(\text{salen})\}_2\text{Mo}_2\text{S}_7]$, (d) $[\{\text{Fe}(\text{salphen})\}_2\text{O}]$, (e) $[\{\text{Fe}(\text{salphen})\}_2\text{Mo}_2\text{O}_7] + 3[\text{MoO}_2(\text{salphen})]$, and (f) $[\{\text{Fe}(\text{saliden})\}_2\text{MoO}_4]$

assignments, are shown in Figure 1. By comparing the spectra of the molybdato-bridged complexes with the spectra of oxo-, thio-, and thiomolybdato-bridged complexes we can distinguish between ligand bands and MoO bands. For the $[\text{MoO}_4]^{2-}$ ion (T_d symmetry) there is a strong band at *ca.* 820 cm^{-1} assigned to an Mo-O stretching vibration (ν_3). When molybdate behaves as a bridging ligand the symmetry of the ion is lowered and the number of i.r. bands increases. Bands assigned to stretching vibrations involving terminal oxygen atoms are shifted to higher wavenumbers than in the free ion.¹² The presence of higher-wavenumber bands in the molybdato complexes is evidence for the presence of bridging molybdate. When molybdate bridges through one oxygen (C_{3v}) three i.r. bands (ν_1 , ν_2 , and ν_4) are expected. For bridging through two oxygens (C_{2v}) four bands (ν_1 , ν_2 , ν_6 , and ν_8) are expected.¹³

For the complexes $[\{\text{Fe}(\text{salen})\}_2\text{MoO}_4]$ and $[\{\text{Fe}(\text{saliden})\}_2\text{MoO}_4]$ there are, in addition to the ligand bands, four bands (900, 850, 810, and 790; 900, 855, 805, and 790 cm^{-1} respectively) which we assign to MoO vibrations. Therefore we consider that in these complexes molybdate bridges between two oxygen atoms. In the spectrum of $[\text{Fe}_3\text{Mo}_5\text{O}_{13}(\text{salphen})_5]$ there were MoO

complexes.⁹ The band is not a ligand band and we assign it to a vibration of the Fe_2O group.

The far-i.r. spectra ($<650 \text{ cm}^{-1}$) are complicated by the presence of ligand bands. For the complex $[\{\text{Fe}(\text{salen})\}_2\text{Mo}_2\text{S}_7]$ there is a band at 490 cm^{-1} which is probably a Mo-S vibration of the bridging Mo_2S_7 group.¹⁴

Magnetic Properties.—Plots of magnetic moment against temperature are given in Figure 2. Magnetic properties are summarised in the Table. The magnetic

Magnetic properties and Mössbauer spectra *

Complex	m/m_B	J/cm^{-1}	$\delta/\text{mm s}^{-1}$	$\Delta/\text{mm s}^{-1}$
$[\{\text{Fe}(\text{salen})\}_2\text{O}]$	1.9	-95	0.32	0.72
$[\{\text{Fe}(\text{salen})\}_2\text{MoO}_4]$	5.6	-5	0.38	1.25
$[\{\text{Fe}(\text{salen})\}_2\text{Mo}_2\text{S}_7]$	4.5		0.38	0.74
			0.48	0.96
$[\{\text{Fe}(\text{salphen})\}_2\text{Mo}_2\text{O}_7]$	5.9	0	0.37	0.75
$[\{\text{Fe}(\text{saliden})\}_2\text{MoO}_4]$	5.8	-1.0	0.37	0.22

* Magnetic moments $m/m_B = \text{constant} \times (\chi_m T)^{\frac{1}{2}}$, exchange integrals (J), and chemical shifts (δ) relative to pure iron, and nuclear quadrupole splittings (Δ) at *ca.* 293 K.

moments of $[\{\text{Fe}(\text{salen})\}_2\text{MoO}_4]$, $[\text{Fe}_3\text{Mo}_5\text{O}_{13}(\text{salphen})_5]$, and $[\{\text{Fe}(\text{saliden})\}_2\text{MoO}_4]$ approach the value (5.9 B.M.) * for high-spin Fe^{III} ($S = \frac{5}{2}$) and decrease slightly with temperature as a result of antiferromagnetic coupling of

¹³ W. M. Reiff, W. A. Baker, and N. E. Erikson, *J. Amer. Chem. Soc.*, 1968, **90**, 4794; W. M. Reiff, G. J. Long, and W. A. Baker, *ibid.*, p. 6347.

¹⁴ D. M. Adams, 'Metal-Ligand and Related Vibrations,' Edward Arnold, London, 1967, p. 317.

* 1 B.M. $\approx 9.27 \times 10^{-24} \text{ A m}^2$.

¹⁰ K. Ueno and A. E. Martell, *J. Phys. Chem.*, 1956, **60**, 1270.

¹¹ P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103.

¹² P. C. H. Mitchell and F. Trifiro, *J. Chem. Soc. (A)*, 1970, 3183.

electron spins on adjacent iron(III) atoms. Values of the exchange integral, J , calculated for the best fit to reciprocal temperature against susceptibility curves, are given in the Table.¹⁵ The magnetic coupling in these complexes is much less than in the oxo- and thio-bridged complexes [$\{\text{Fe}(\text{salen})\}_2\text{O}$]^{15,16} and [$\{\text{Fe}(\text{salen})\}_2\text{S}$].⁹ Although the magnetic moment (4.55 B.M.) of [$\{\text{Fe}(\text{salen})\}_2\text{Mo}_2\text{S}_7$] is below the spin-only value for Fe^{III} ($S = \frac{5}{2}$), the variation with temperature is slight (Figure 2). The low moment cannot be explained by interactions between the iron atoms and must therefore be

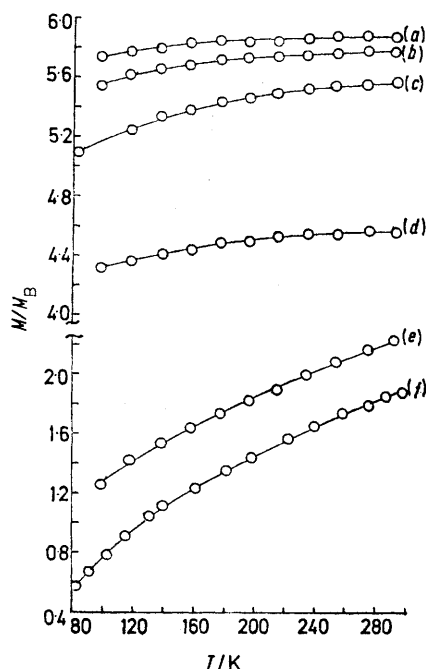


FIGURE 2 Variation of magnetic moment with temperature for (a) [$\{\text{Fe}(\text{salphen})\}_2\text{Mo}_2\text{O}_7$], (b) [$\{\text{Fe}(\text{saliden})\}_2\text{MoO}_4$], (c) [$\{\text{Fe}(\text{salen})\}_2\text{MoO}_4$], (d) [$\{\text{Fe}(\text{salen})\}_2\text{Mo}_2\text{S}_7$], (e) [$\{\text{Fe}(\text{salen})\}_2\text{S}$], and (f) [$\{\text{Fe}(\text{salen})\}_2\text{O}$]

due to a change of spin state of the iron. Possible spin states are $S = \frac{3}{2}$ (spin-only moment 3.87 B.M.) as found for certain five-co-ordinate dithiocarbamate-complexes, e.g. [$\text{Fe}(\text{S}_2\text{CNET}_2)\text{Cl}$]¹⁷ and $S = \frac{1}{2}$ (μ ca. 2.0 B.M.). Since the magnetic moment of [$\{\text{Fe}(\text{salen})\}_2\text{Mo}_2\text{S}_7$] changes only from 4.55 at 293 K to 4.32 B.M. at 99 K the spin state $S = \frac{1}{2}$ is unlikely and the most plausible explanation of the magnetic properties is the presence of Fe^{III} in spin states $S = \frac{3}{2}$ and $\frac{5}{2}$, the latter becoming more populated as the temperature rises.¹⁸

Mössbauer Spectra.—The isomer shifts, δ , and the nuclear quadrupole splittings, Δ , are given in the Table. Values of δ are in the range 0.3–0.4 mm s⁻¹ which is

characteristic of the $S = \frac{5}{2}$ spin state.^{7,13} For [$\{\text{Fe}(\text{salen})\}_2\text{Mo}_2\text{S}_7$] there was a shoulder on the main absorption peak at δ ca. 0.48 mm s⁻¹ which is of the order expected for $S = \frac{3}{2}$ iron.¹⁹ The nuclear quadrupole splitting (1.25 mm s⁻¹) for [$\{\text{Fe}(\text{salen})\}_2\text{MoO}_4$] is greater than for [$\{\text{Fe}(\text{salen})\}_2\text{O}$], and is closer to the value (1.40 mm s⁻¹) for [$\{\text{FeCl}(\text{salen})\}_2$] in which the two $\text{Fe}(\text{salen})$ units are bridged through oxygen atoms of the Schiff bases and the iron is six-co-ordinate.²⁰ For [$\{\text{Fe}(\text{saliden})\}_2\text{MoO}_4$] the Δ value is much less than for the other complexes. This complex differs from the others in that the Schiff base ligand is quinquedentate whereas in the other complexes the ligands are quadridentate. Thus it seems that the combination of a quinquedentate ligand and bridging molybdate reduces the asymmetry of the electric-field gradient, giving a small Δ value.

Electronic Spectra.—The electronic spectra consisted of broad bands with ill defined peaks extending through the visible region. Peaks at $>25\,000\text{ cm}^{-1}$ are assigned to ligand internal transitions by comparison with the spectra of the Schiff bases. In the spectrum of [$\{\text{Fe}(\text{salen})\}_2\text{MoO}_4$] there was an additional intense band at $22\,000\text{ cm}^{-1}$, assigned to a Schiff base-to-iron(III) charge-transfer transition, and in the spectrum of [$\{\text{Fe}(\text{salen})\}_2\text{Mo}_2\text{S}_7$] a band at $20\,500\text{ cm}^{-1}$ which is probably a $\text{S} \rightarrow \text{Fe}^{\text{III}}$ charge-transfer transition (cf. the $19\,600\text{ cm}^{-1}$ band of [$\{\text{Fe}(\text{salen})\}_2\text{S}$]).⁹ Charge-transfer transitions were not observed for [$\{\text{Fe}(\text{salen})\}_2\text{O}$] presumably because they are at greater wavenumber than in the molybdate complexes and obscured by the ligand absorptions. For the molybdate-bridged complexes as for [$\{\text{Fe}(\text{salen})\}_2\text{O}$] there was a weak band at $9\,500\text{ cm}^{-1}$ assigned to a $d-d$ transition of Fe^{III} . The intensities were greater for the oxo-bridged complexes than for the molybdate complexes in agreement with the view that the intensities of formally spin-forbidden bands are enhanced in systems of magnetically interacting ions.²¹

Conclusions.—We have shown that molybdate and thiomolybdate anions can act as bridging ligands in binuclear iron(III) Schiff-base complexes. The spin coupling between iron atoms is much less in these complexes than in the analogous oxo- and thio-bridged complexes and so, although the complexes are binuclear, their magnetic and spectroscopic properties correspond to those of mononuclear iron(III) complexes. There is evidence for Fe^{III} in spin states $S = \frac{3}{2}$ and $\frac{5}{2}$ in [$\{\text{Fe}(\text{salen})\}_2\text{Mo}_2\text{S}_7$].

Our results are of particular interest in the context of iron-molybdenum relations in biological systems since they indicate that molybdate (and possibly other anions) can bind in the axial position of iron in, for example, haem proteins (for which the Schiff-base complexes have been regarded as models⁷).

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¹⁶ J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. (A)*, 1967, 1014.

¹⁷ R. L. Martin and A. H. White, *Inorg. Chem.*, 1967, 6, 712.

¹⁸ R. L. Martin and A. H. White, *Transition Metal Chem.*, 1968, 4, 113.

¹⁹ T. Birchall, *Canad. J. Chem.*, 1969, 47, 4563.

²⁰ M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, *Nature*, 1966, 212, 809.

²¹ J. Ferguson, H. J. Guggenheim, and Y. Tanabe, *J. Phys. Soc. Japan*, 1966, 21, 692; J. A. Bertrand and P. G. Eller, *Inorg. Chem.*, 1974, 13, 927.