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Transmetalation of Tetranuclear Copper(I) Complexes with an $Fe(NS)_3$ Reagent*

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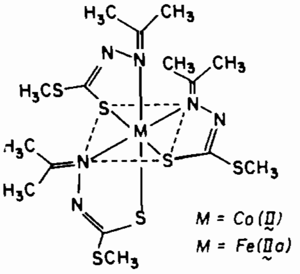
Abstract

Stoichiometric transmetalation of tetranuclear copper(I) complexes $N_4Cu_4X_4$ (**I**; N = *N,N*-diethylnicotinamide; X = Cl or Br) by 1 mol or excess tris(*S*-methyl isopropylidenehydrazinecarbodithioato)iron(III) ($Fe(NS)_3$, **IIa**) in aprotic solvents under dinitrogen is preceded by electron transfer from copper(I) to iron(III) and gives tetranuclear iron(II)-containing products: **I** + **IIa** $\rightarrow N_4Cu_2{}^{I}Cu^{II}Fe^{II}(NS)_2X_4$ (**III′**) + Cu(NS)(s). The rates of reaction of **I** with $M(NS)_3$ and $M(NS)_2$ reagents (M = Co, Ni, Cu, Zn) decrease in the order $Co(NS)_3$ (**II**) > **IIa** > $M(NS)_2$. Products **III′** react stoichiometrically with 1 mol of **II** or $M(NS)_2$ or with 2 mols of **II** or $M(NS)_2$ to give iron(III)-containing dimers $N_4MFe(OH)X_4$ (**VIII′**) and trimers $N_3M_2Fe(OH)X_4O$ (**X′**), respectively, after oxidation with dioxygen and isolation. Transmetalation of **III′** with equimolar mixed transmetalators $M(NS)_2$ and $M'(NS)_2$ is selective but gives dimers $N_4MM'X_4$ instead of **VIII′** because $Fe(NS)_2$ is more thermodynamically stable than $M'(NS)_2$. Aprotic oxidation of **III′** by dioxygen proceeds in two distinct stages, the first corresponding to four-electron oxidation of the two copper(I) and two coordinated NS ligands of **III′** and the second to oxidation of the iron(II) center of **III′**. The isolated oxidation products are $(\mu_4\text{-O}, \mu\text{-O})N_4Cu_3Fe(OH)X_4$ (**IV′**). Products **IV′** characteristically lose 1 mol CuO on transmetalation with 2 mol of $M(NS)_2$ or **II** to give trimers **X′**. Products **IV′** also react with 1 or 2 mol of $Fe(NS)_3$ to give trimers $(\mu_3\text{-O})N_3Fe(OH)CuFe(NS)X_4$ (**XI′**) and $(\mu_3\text{-O})N_3Fe(OH)(Fe(NS))_2X_4$ (**XII′**), respectively. The major differences between $Co(NS)_3$ and $Fe(NS)_3$ as transmetalators of **I**, **III′** and **IV′** are (i) lack of reaction of **III** and **III′** with excess $Fe(NS)_3$; (ii) facile oxidation of iron(II) in transmetalated products by dioxygen; (iii) case of transmetalation of these iron(II) centers with $M(NS)_2$; (iv) stability of Fe(NS) centers in transmetalated products **XI′** and **XII′**.

Introduction

We are engaged in a systematic investigation of the scope and characteristics of transmetalation, a route to many new heteropolymetallic complexes that have not been obtained by other means [2–12].

Scheme 1 summarizes transmetalation of copper(I) and copper(II) centers by $Co(NS)_3$ (**II**) and $M(NS)_2$ reagents. Here, N is monodentate *N,N*-diethylnicotinamide (DENC), X is Cl or Br, M is Co, Ni, Cu or Zn and NS is monanionic *S*-methyl isopropylidenehydrazinecarbodithioate. All the reactions proceed readily and stoichiometrically in aprotic solvents at room temperature and the polynuclear transmetalation products are easily isolated [3, 4].



The most important features of Scheme 1 [3, 4] are: (i) transmetalation of $N_4Cu_4X_4$ (**I**) by **II** is preceded by electron transfer: as a result, all the products contain cobalt(II), which is not oxidized by dioxygen in the ligand systems shown; (ii) the transmetalation reactions are driven by the high thermodynamic stability of Cu(NS)(s) and $Cu(NS)_2$ coproducts; (iii) Cu(NS)(s) precipitation is a useful means of gravimetric stoichiometry measurement that indicates preferential transmetalation of copper(I) in **III** by $M(NS)_2$; (iv) all the heteropolynuclear products shown can be obtained by simultaneous transmetalation: for example, **VIII** are obtained by reacting **I** with equimolar **II** and $M(NS)_2$; (v) transmetalation is not limited to copper-containing reactants: for example, **VI** and **VIII** in Scheme 1 can be interconverted with appropriate $M(NS)_2$ reagents because of stability differences $Cu(NS)_2 > Ni(NS)_2 > Co(NS)_2 > Zn(NS)_2$: these

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*Taken in part from ref. 1.

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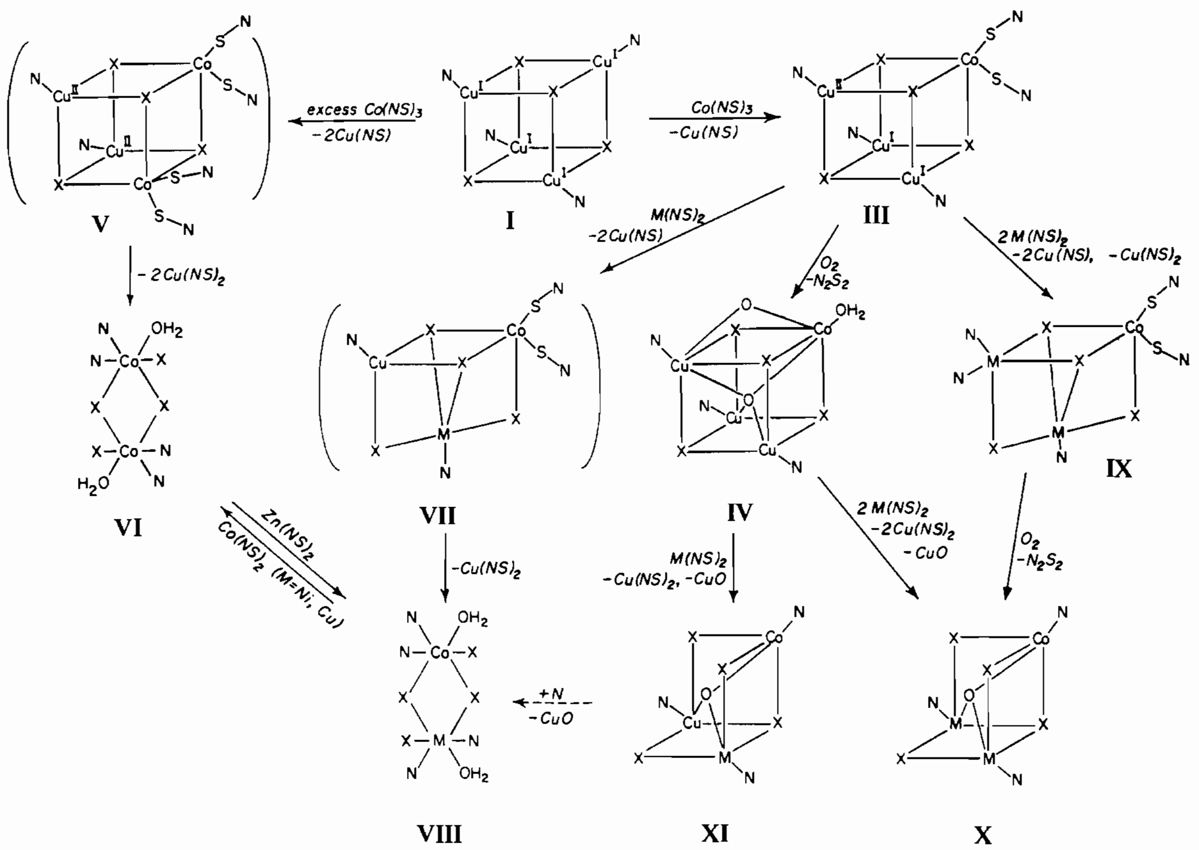

Scheme 1.

differences also lead to selective transmetalation of **III** to **VIII** by equimolar $M(NS)_2$ and $M'(NS)_2$; (vi) species **III** are four-electron reducing agents containing two formal copper(I) centers and two coordinated NS ligands that are oxidized to copper(II) in **IV** and the disulfide N_2S_2, respectively, by dioxygen; (vii) complexes **IV** (M = Co, Ni or Zn) are sources of trimers **X** containing up to three different metals; (viii) transmetalation of the copper(II) centers in **IV** with $Co(NS)_3$ also gives coproducts CuO and $Cu(NS)_2$ but the resulting $Co^{III}(NS)$ centers self-destruct to give Co^{II} in **X** and the disulfide N_2S_2 [3, 4].

Establishment of Scheme 1 led us to explore the corresponding reactions of $Fe(NS)_3$ (**IIa**) for comparative purposes and because iron and copper have such special roles in biochemical catalytic systems [13, 14], for example in cytochrome oxidase [15].

This paper reports that **I** reacts stoichiometrically with $Fe(NS)_3$ (**IIa**) and $M(NS)_2$ transmetalators to give polynuclear iron-containing products that are primed in Scheme 2 to facilitate comparison with Scheme 1. Major differences between the Schemes are that (i) **III′** does not react with **IIa** to give the dimeric analog of **VI** (Scheme 1); (ii) species **III′** are five-electron reducing agents because their iron(II) centers are oxidized by dioxygen; (iii) isolated heterodimers **VIII′** are iron(III) complexes for the same reason; (iv) transmetalation of copper(II) in **IV′** by **IIa** is slower than with **II** because **IIa** is more thermodynamically stable; (v) the resulting Fe(NS) centers do not self-destruct.

Experimental

Most of the reagents, synthetic procedures, product isolation techniques, analytical methods and physical measurements employed in this work have been described previously [2–12].

*Tris-(S-methyl isopropylidenehydrazinecarbodithioato)iron(III), $Fe(NS)_3$ (**IIa**)*

Neutral transmetalating agent tris(*S*-methyl isopropylidenehydrazinecarbodithioato)iron(III) ($Fe(NS)_3$, **IIa**) was obtained as follows. A suspension of iron(II) acetate (Alfa) in ethanol was treated with excess dioxygen at room temperature for 30 min*.

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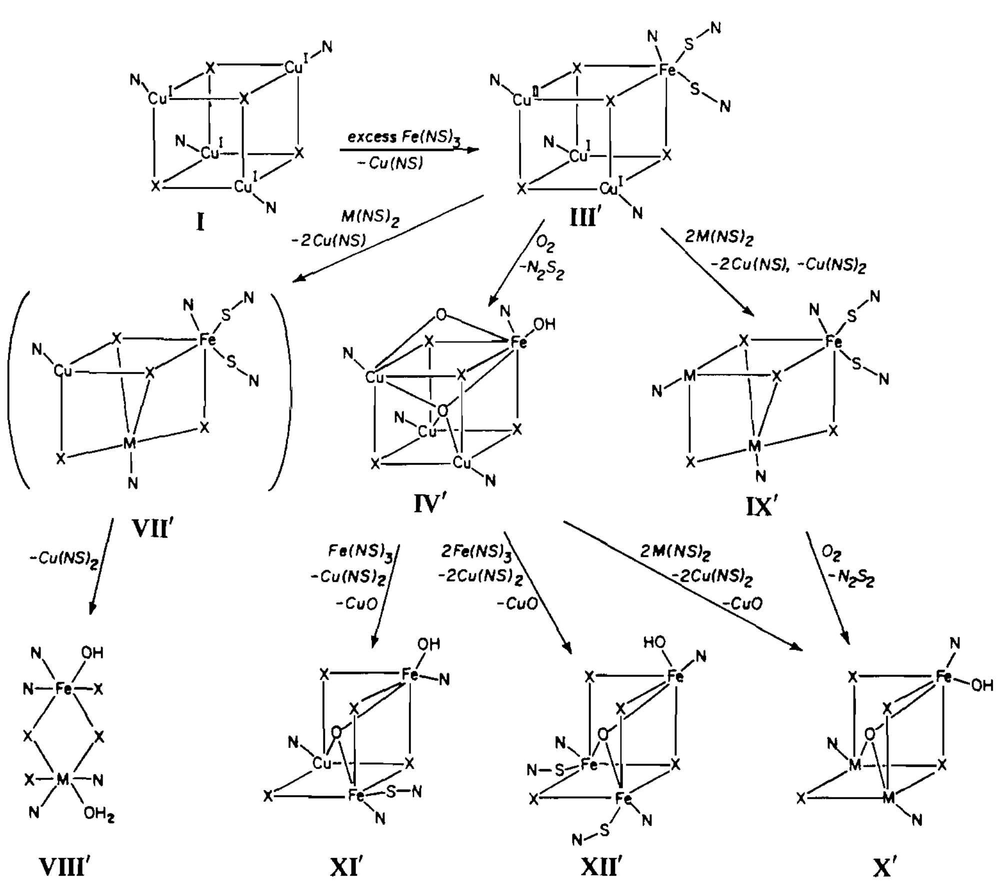
*Preoxidation of iron(II) acetate is necessary to obtain any useful products from this reaction. Iron(II) acetate does not react with 2 mol of HNS to give $Fe(NS)_2$ in refluxing alcohols. Other methods of $Fe(NS)_2$ synthesis are being investigated.



Scheme 2.

The dark brown product solution was treated with 3 mol HNS and refluxed for 30 min. The gray solid that formed in *c.* 85% yield on cooling to room temperature was washed with ethanol and dried under vacuum at room temperature. Its iron content was determined by plasma emission spectroscopy at 333.40 nm (detection limit 50 ng/ml) after standard sample preparation [4]. *Anal.** Found: C, 34.3; H, 5.1; N, 16.1; S, 36.3; Fe, 10.3. Calc. for $FeC_{15}H_{27}N_6S_6$: C, 33.68; H, 5.04; N, 15.57; S, 35.62; Fe, 10.35%. M_r (by cryoscopy in nitrobenzene) 520 ± 20 g/mol (539).

Stoichiometric transmetalation reactions were conducted sequentially [3] or simultaneously [4] in methylene chloride or nitrobenzene under dinitrogen and were generally complete after 12 or 24 h at room temperature. Some slower reactions are specified in the text. Heteropolymetallic transmetalation products were isolated from methylene chloride by gel permeation chromatography (Biobeads SX-12 resin, methylene chloride eluant) after treatment with dioxygen [2–4] or by addition of product filtrates in nitrobenzene to an equal volume of anhydrous hexane at room temperature under dinitrogen [4, 11]. Analytical data are collected in Tables 1 and 2.

Mössbauer spectra of $Fe(NS)_3$ and iron-containing transmetalation products were obtained on a Camberra Series 35 multichannel analyzer operating in a time mode in conjunction with a constant acceleration linear drive motor. The gamma ray source was ^{57}Co in a rhodium metal matrix. Isomer shifts and quadrupole splittings are quoted relative to metallic iron at room temperature. Least-squares Lorentzians were fitted to the spectra by the method of Stone *et al.* [16], which provides statistical goodness of fit and reliability estimates.

Results and Discussion

Synthesis and Properties of Fe(NS)$_3$

Neutral transmetalating agent $Fe(NS)_3$ (**IIa**; NS is *S*-methyl isopropylidenehydrazinecarbodithioate) is obtained in high yield as a gray solid by reaction of a preoxidized suspension of iron(II) acetate with three equivalents of HNS in refluxing ethanol. The synthesis is complete within 30 min under these conditions and gives an analytically pure, monomeric product (see 'Experimental').

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*C, H, N and S analyses were made by Galbraith Laboratories, Knoxville, TN.

TABLE 1. Analytical data for transmetalated products[a]

Reaction	Symbol[b]	Complex	Analysis (%)									M_r[c]
			C	H	N	X	Fe	Co	Ni	Cu	Zn	
4	**IIIa′**	$N_4Cu_3Fe(NS)_2Cl_4$	41.9 (42.16)	4.9 (5.17)	11.3 (11.81)	9.2 (9.96)	4.9 (3.94)			12.9 (13.38)		1380 ± 20 (1423)
4	**IIIb′**	$N_4Cu_3Fe(NS)_2Br_4$	36.8 (37.48)	4.2 (4.59)	10.1 (10.49)	18.9 (19.98)	4.5 (3.49)			11.3 (11.89)		1520 ± 20 (1601)
21, 22	**IVa′**	$N_4Cu_3Fe(OH)Cl_4O_2$	41.1 (41.74)	4.6 (4.99)	9.5 (9.74)	11.9 (12.33)	5.6 (4.87)			16.3 (16.56)		1095 ± 20 (1150)
21, 22	**IVb′**	$N_4Cu_3Fe(OH)Br_4O_2$	36.4 (36.12)	4.2 (4.32)	8.2 (8.43)	23.8 (24.08)	3.8 (4.21)			14.3 (14.33)		1290 ± 20 (1329)
8	**VIIIa′**	$N_4Fe(OH)CoCl_4 \cdot H_2O$	47.2 (47.76)	5.7 (5.92)	10.9 (11.14)	14.4 (14.11)	4.8 (5.57)	5.1 (5.87)				1045 ± 20 (1005)
8	**VIIIb′**	$N_4Fe(OH)NiCl_4 \cdot H_2O$	47.5 (47.76)	5.8 (5.92)	11.0 (11.14)	13.5 (14.11)	5.3 (5.57)		4.9 (5.87)			940 ± 20 (1005)
8	**VIIIc′**	$N_4Fe(OH)CuCl_4 \cdot H_2O$	47.4 (47.57)	5.3 (5.89)	10.8 (11.10)	13.3 (14.05)	5.9 (5.55)			6.1 (6.29)		980 ± 20 (1009)
8	**VIIId′**	$N_4Fe(OH)ZnCl_4 \cdot H_2O$	47.1 (47.48)	5.3 (5.88)	10.2 (11.08)	13.8 (14.03)	4.9 (5.54)				6.2 (6.46)	950 ± 20 (1011)
8	**VIIIa′**[d]	$N_4Fe(OH)CoCl_4 \cdot H_2O$	47.2 (47.76)	5.7 (5.92)	10.4 (11.14)	13.9 (14.11)	4.7 (5.57)	5.3 (5.87)				960 ± 20 (1005)
11	**IXb′**	$N_3Ni_2Fe(NS)_2Cl_4$	38.6 (39.70)	3.8 (4.71)	8.8 (9.26)	10.1 (11.72)	3.8 (4.63)		9.4 (9.76)			1170 ± 20 (1209)
11	**Xa′**[d, e]	$N_3Fe(OH)Co_2Cl_4O$	38.9 (39.13)	4.3 (4.71)	8.9 (9.13)	15.2 (15.41)	5.9 (6.08)	12.6 (12.83)				1020 ± 20 (920)
11	**Xb′**[e]	$N_3Fe(OH)Ni_2Cl_4O$	39.1 (39.13)	4.8 (4.71)	9.1 (9.13)	15.6 (15.41)	6.1 (6.08)		12.4 (12.83)			1000 ± 20 (920)
11	**Xc′**[e]	$N_3Fe(OH)Cu_2Cl_4O$	37.2 (38.75)	3.9 (4.66)	8.1 (9.04)	14.1 (15.26)	5.1 (6.03)			12.41 (13.67)		960 ± 20 (929)

[a] Calculated values in parentheses. [b] See Scheme 2. [c] Measured cryoscopically in nitrobenzene at (3–5) × 10^{-2} m. [d] From simultaneous reaction of **I** with **IIa** and $Co(NS)_2$. See text. [e] Obtained after aprotic oxidation of **IX′** with O_2 and gel permeation chromatography (eqns. (18) and (20)). See text.

TABLE 2. Analytical and cryoscopic data for products of reaction of $N_4Cu_3Fe(NS)_2Cl_4$ (IIIa′) and $N_4Cu_3Fe(OH)Cl_4O_2$ (IVa′) with equimolar $M(NS)_2$ and $M'(NS)_2$ reagents[a]

Reaction	M, M′	Product (M)[b]	Analysis (%)										M_r[c]
			C	H	N	S	Cl	Fe	Co	Ni	Cu	Zn	
(i) Reactions of IIIa′													
9	IIa, Co	VIIIa′	47.9 (47.76)	6.1 (5.92)	11.2 (11.14)		14.3 (14.11)	5.2 (5.57)	5.9 (5.87)				970 ± 20 (1005)
9	IIa, Ni	VIIIb′	47.3 (47.76)	5.6 (5.92)	10.8 (11.14)		13.3 (14.11)	5.4 (5.57)		5.6 (5.87)			1050 ± 20 (1005)
9	IIa, Zn	VIIId′	47.1 (47.48)	5.4 (5.88)	10.1 (11.08)		13.7 (14.03)	5.2 (5.54)				5.99 (6.46)	950 ± 20 (1011)
16	Co, Co	$N_4Co_2Cl_4 \cdot 2H_2O$	46.0 (46.51)	6.1 (5.99)	10.8 (11.11)		13.5 (14.06)		11.5 (11.69)				1030 ± 20 (1009)
16	Co, Ni	$N_4CoNiCl_4 \cdot H_2O$	47.2 (47.76)	5.7 (5.99)	11.2 (11.11)		13.7 (14.06)		5.3 (5.9)	6.5 (5.0)			890 ± 20 (1009)
16	Co, Zn	$N_4CoZnCl_4 \cdot H_2O$	46.8 (47.29)	5.2 (5.96)	10.7 (11.03)		13.3 (13.97)		5.2 (5.81)			7.1 (6.43)	990 ± 20 (1015)
(ii) Reactions of IVa′													
23	Co, Co	Xa′ (Co)	38.7 (39.13)	3.5 (4.71)	8.9 (9.13)		14.5 (15.41)	5.9 (6.08)	12.3 (12.83)				870 ± 20 (920)
23	Ni, Ni	Xb′ (Ni)	38.5 (39.13)	4.3 (4.71)	9.4 (9.13)		15.9 (15.41)	6.3 (6.08)		12.2 (12.83)			1020 ± 20 (920)
23	Zn, Zn	Xd′ (Zn)	37.9 (38.59)	4.3 (4.65)	8.8 (9.00)		14.4 (15.19)	5.1 (6.00)				12.89 (13.93)	920 ± 20 (933)
23	Co, Ni	Xe′ (Co, Ni)	38.9 (39.13)	4.6 (4.71)	8.7 (9.13)		14.8 (15.41)	5.8 (6.08)	5.7 (6.41)	5.9 (6.41)			1000 ± 20 (920)
27	IIa	XI′	39.8 (40.15)	4.8 (5.01)	10.4 (10.71)	5.7 (6.12)	13.9 (10.71)	9.9 (10.71)			5.7 (6.07)		1070 ± 20 (1046)
28	IIa, IIa	XII′	39.5 (40.00)	4.9 (5.12)	11.3 (11.67)	10.3 (10.67)	10.7 (11.82)	13.5 (14.00)					d (1200)

[a] Analytical data are given for desired polynuclear products separated after oxidation with dioxygen by gel permeation chromatography in each system. Calculated values in parentheses. [b] Symbols in Scheme 2; product identification in Table 1 and text. [c] Measured cryoscopically in nitrobenzene at (3–5) × 10^{-2} m. [d] Not soluble in nitrobenzene. See text.

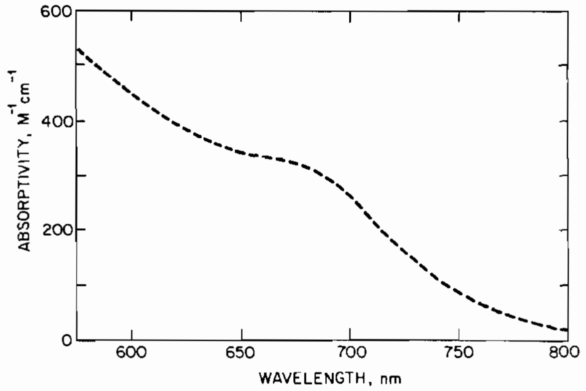

Fig. 1. Electronic spectrum of $Fe(NS)_3$ (**IIa**) in methylene chloride at 25 °C.

The room temperature Mössbauer isomer shift (0.23 ± 0.01 mm/s) and quadropole splitting (0.55 ± 0.03 mm/s) confirm that solid **IIa** is an iron(III) complex [17]. A sharp band at 1000 cm^{-1} in its IR spectrum identifies bidentate NS^- [18–21]. The room temperature electronic spectrum of **IIa** in methylene chloride (Fig. 1) consists of a very broad band centered at 680 nm (ϵ 330 M^{-1} cm^{-1}) that is typical of neutral, high-spin iron(III) complexes [22].

Like other neutral $M(NS)_n$ complexes, **IIa** is highly soluble in aprotic solvents, which makes it very suitable for large scale transmetalations of neutral copper complexes. Neutrality and high solubility of $M(NS)_n$ are impediments to single crystal growth; nevertheless, a number have been crystallized and their structures determined [21a–c]: for example, $Co(NS)_3$ (II) crystallizes as the green, monomeric *fac*-isomer [21d].

Despite many attempts, we were unsuccessful in crystallizing monomeric **IIa** intact. However, a brown, crystalline solid **IIb** was obtained in high yield by slow evaporation of methylene chloride data (*Anal.* for **IIb**. Found: C, 31.5; H, 4.7; N, 14.6; S, 32.6; Fe, 13.9. Calc. for $FeC_{10}H_{19}N_4S_4O$: C, 31.41; H, 4.85; N, 14.19; S, 32.47; Fe, 14.14%. M_r = 765 ± 20 (788) by cryoscopy in nitrobenzene) and a crystal structure determination [23] have identified **IIb** as the five-coordinate oxoiron(III) dimer $[Fe(NS)_2]_2O$, whose structure, properties and transmetalation reactions will be described separately [23]. For present purposes we note that while solid $Fe(NS)_3$ (**IIa**) is very stable, its aprotic solutions are subject to slow decomposition, presumably via eqn. (1). For this reason, all transmetalations were run under dinitrogen with freshly prepared aprotic solutions of **IIa**.

$$\underset{\textbf{IIa}}{2Fe(NS)_3} + 0.5O_2 \longrightarrow [Fe(NS)_2]_2O + N_2S_2 \qquad (1)$$

Transmetalations with $Co(NS)_3$ (II) and $Fe(NS)_3$ (IIa): General Observations

Schemes 1 and 2 summarize the different patterns of transmetalation of copper(I) and copper(II) centers by $Co(NS)_3$ (**II**) [3, 4] and $Fe(NS)_3$ (**IIa**) respectively. Analogous products are primed in Scheme 2 to facilitate comparison.

The pale yellow, insoluble coproduct Cu(NS)(s) of copper(I) transmetalation by (*S*-methyl isopropylidenehydrazinecarbodithioato)metal complexes can be isolated and weighed to establish reaction times and stoichiometries [2–4, 24].

Gravimetric measurements showed that copper(I) complexes **I** are stoichiometrically transmetalated by **II** [3, 4] and **IIa** within 12 h under typical [3, 4] experimental conditions. Spectrophotometric monitoring of the black coproduct $Cu(NS)_2$ of copper(II) transmetalation by **IIa** indicated that 24 h is sufficient to ensure complete, stoichiometric reaction at room temperature in all cases. This is 3–10 times longer than required for analogous copper(II) transmetalations with $M(NS)_2$ (M = Co, Ni, Zn) and **II** [2–10], consistent with the high relative thermodynamic stability of **IIa** (see below).

Relative Stability of $Fe(NS)_3$

Irreversible reaction (2) in ethanol indicates that $Co(NS)_2$ is much more thermodynamically stable than $Zn(NS)_2$ [4].

$$CoCl_2 + Zn(NS)_2 \longrightarrow Co(NS)_2 + ZnCl_2 \qquad (2)$$

Similar experiments were used to establish a decreasing order of stabilities $Cu(NS)_2 > Ni(NS)_2 > Co(NS)_2 > Co(NS)_3 > Zn(NS)_2$ with fixed NS [4]. We know the stability order $Cu(NS)_2 > Fe(NS)_3$ from the fact that halocopper(II) centers are stoichiometrically transmetalated by $Fe(NS)_3$ to give coproduct $Cu(NS)_2$ (see text and Scheme 2). The electronic spectrum of a solution of equimolar $Fe(NS)_3$ and $NiCl_2$ in ethanol under dinitrogen was invariant for at least 24 h at room temperature. Thus, the transmetalator stability order is $Cu(NS)_2 > Fe(NS)_3 > Ni(NS)_2 > Co(NS)_2 > Co(NS)_3 > Zn(NS)_2$. This order helps to explain the results of competitive transmetalation of **III′** by mixed transmetalators $M(NS)_2$ and $M'(NS)_2$, in particular that iron centers can be transmetalated with $Ni(NS)_2$, $Co(NS)_2$ and $Zn(NS)_2$ (see below).

Transmetalation of I with Equimolar $Fe(NS)_3$ (IIa)

An immediate color change to very dark greenish-brown was observed on dropwise addition of one equivalent of a brown solution of $Fe(NS)_3$ (**IIa**) to pale yellow **I** in methylene chloride or nitrobenzene under dinitrogen. Corresponding experiments with $Co(NS)_3$ (**II**) result in deep blue colors characteristic of cobalt(II) [3, 4]. Both color changes were much faster than the subsequent, slow precipitation of 1 mol of Cu(NS)(s), eqns. (3) and (4), establishing that electron transfer from copper(I) in **I** to cobalt(III) or iron(III) in $M(NS)_3$ precedes transmetalation.

$$\mathbf{I} + Co(NS)_3 \longrightarrow \underset{\mathbf{III}}{N_3Cu_3Co(NS)_2X_4} + N + Cu(NS)(s) \qquad (3)$$

$$\mathbf{I} + Fe(NS)_3 \longrightarrow \underset{\mathbf{III'}}{N_4Cu_3Fe(NS)_2X_4} + Cu(NS)(s) \qquad (4)$$

The filtrates from experiments in nitrobenzene were examined cryoscopically and the transmetalation products were then precipitated by addition to excess deoxygenated hexane. The filtrates from eqn. (3) contain equimolar **III** and N [3,4]; by contrast, cryoscopic data indicated no free N in the filtrates from eqn. (4) and the isolated tetranuclear products **III′** contain four N ligands (Table 1). Iron evidently has a much higher affinity for N than other metals M = Co, Ni, Cu, Zn in $N_3Cu_3M(NS)_nX_4$ complexes [2–4].

Electron Distribution in III and III′

Species **III**, Scheme 1, under dinitrogen exhibit pronounced electronic spectral features at 610 and 850 nm, indicating the presence of cobalt(II) and copper(II), respectively, in the designation $N_3Cu^I{}_2Cu^{II}Co^{II}(NS)_2X_4$ (see ref. 4, Fig. 1). Negligible absorption at 850 nm in products $N_3Cu^I{}_3M(NS)X_4$ from eqn. (5) (M = Co, Ni, Zn) confirms the absence of copper(II) in cases where intramolecular electron transfer from copper(I) to M^{II} is not expected. The similarity of $\epsilon_{850} = (600 \pm 20)\ M^{-1}\ cm^{-1}$ for $N_3Cu_3Co(NS)_2Cl_4$ (**IIIa**) (ref. 4, Fig. 1) and $\epsilon_{850} = (525 \pm 20)\ M^{-1}\ cm^{-1}$ for $N_4Cu_3Fe(NS)_2Cl_4$ (**III′a**) (Fig. 2),

$$\mathbf{I} + M(NS)_2 \longrightarrow N_3Cu^I{}_3M(NS)X_4 + N + Cu(NS)(s) \qquad (5)$$

suggests the formalism $N_4Cu^I{}_2Cu^{II}Fe^{II}(NS)_2X_4$ for products **III′**. The small difference in ϵ_{850} could be due to the combined effects of (i) significant absorption of the $Fe^{II}(NS)_2X_3$ chromaphore at 850 nm; (ii) different extents of halobridged $M^{II}–Cu^{II}–Cu^I$ electronic coupling that influence the atomic absorptivities of copper(II); (iii) different proportions of $N_nCu^I{}_3M^{III}(NS)_2X_4$ and $N_nCu^I{}_2Cu^{II}M^{II}(NS)_2X_4$ at equilibrium; (iv) experimental error. Within experimental error, the similarity of ϵ_{850} suggests that $N_nCu^I{}_2Cu^{II}M^{II}(NS)_2X_4$ predominate at room temperature when M = Co or Fe.

The electronic spectra of tetranuclear halo(amine)-copper(II) complexes exhibit pronounced minima in the region 500–600 nm [11], while **III′a** has $\epsilon_{600} \approx 900\ M^{-1}\ cm^{-1}$, Fig. 2. We conclude that the formal $Fe^{II}(NS)_2X_3$ chromaphores of **III′** are the primary contributors to this absorption, particularly since iron(III) complex **IIa** has a shoulder at longer wavelength with ϵ_{670} only $310\ M^{-1}\ cm^{-1}$, Fig. 1.

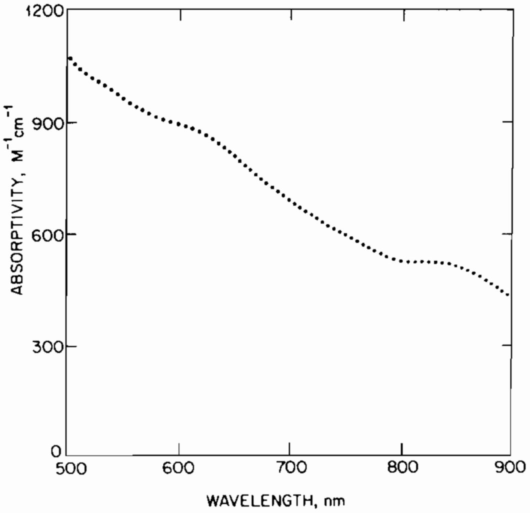

Fig. 2. Electronic spectrum of $N_3Cu_3Fe(NS)_2Cl_4$ (**IIIa′**) in nitrobenzene at 25 °C.

Solids **III′** are extremely air-sensitive; their Mössbauer spectra always indicated various degrees of iron(III) contamination (see below) and were equivocal as a method of iron(II) identification. However, their IR spectra in methylene chloride solution under dinitrogen exhibited sharp, single bands at 1635 cm^{-1}, indicating monodentate coordinated N [2–10]. Sharp bands at 1000 cm^{-1} are observed in complexes containing bidentate NS [18–21]. Products **III** [3,4] and **III′** have broader bands in this region, which suggests monodentate NS coordination; this corresponds to five and six-coordinate cobalt(II) and iron(II) centers in **III** and **III′**, respectively (Schemes 1 and 2). The neutrality and extreme air-sensitivity of solid **III** and **III′** frustrated many attempts to crystallize them intact.

Transmetalation of Copper(I) Complexes I with Excess IIa

Dimers **VI**, Scheme 1, are obtained via **V** from reaction of **I** or **III** with excess **II**, eqns. (6) and (7), respectively [3, 4]. We found from negligible Cu(NS)(s) production that **III**, **III′** and $N_3Cu_3M(NS)X_4$

$$\mathbf{I} + \text{excess}\ \mathbf{II} \longrightarrow \mathbf{VI} + 2Cu(NS)_2 + 2Cu(NS)(s) \qquad (6)$$

$$\mathbf{III} + \text{excess}\ \mathbf{II} \longrightarrow \mathbf{VI} + 2Cu(NS)_2 + Cu(NS)(s) \qquad (7)$$

complexes from eqns. (3)–(5), respectively, do not react at significant rates with up to a five-fold excess of **IIa** at room temperature under dinitrogen and verified that transmetalation of **I** is limited to reactions (4). By contrast, **III′** readily reacts with **II** to give dimers isolated as **VIII′** (M = Co, Scheme 2; see below). $Fe(NS)_3$ is evidently unable to accept an electron from copper(I) in **III**, **III′** or $N_3Cu_3M(NS)X_4$ as a requirement to transmetalate copper(I) [3,4] or to transmetalate the formal copper(II) centers of **III** and **III′** at significant rates.

Simultaneous Transmetalation of I with Equimolar II and IIa

A solution of 0.05 M **I** (X = Cl) in methylene chloride was treated under dinitrogen with a solution containing 0.05 M each of **II** and **IIa** in methylene chloride. Precipitation of 1 mol of Cu(NS)(s) after 4 h indicated the completion of reaction (3) or (4). The filtrate was treated with dioxygen for 15 min and the products **IV** (Scheme 1, X = Cl), $Cu(NS)_2$ and unreacted $Fe(NS)_3$ were immediately separated by gel permeation chromatography [3, 4]*. Exclusive production of **IV**, rather than **IV**′, indicates that **I** is selectively transmetalated by cobalt(III) complex **II**.

Simultaneous or Sequential Transmetalation of I with Equimolar IIa and M(NS)₂

Reactions (8) were observed on treating **I** with equimolar **IIa** and $M(NS)_2$. The dimeric products

$$\mathbf{I} + \mathbf{IIa} + M(NS)_2 \longrightarrow N_4FeMX_4 + 3Cu(NS)(s) + Cu(NS)_2 \qquad (8)$$

were isolated as the iron(III) complexes **VIII**′ after oxidation with dioxygen (Table 1; see below). The same results were obtained in sequence by preforming **III**′ in eqn. (4). The intermediacy of **III**′ in eqn. (8) is confirmed by the fact that $N_3Cu_3M(NS)X_4$ complexes, preformed from eqn. (5) [2], do not react at significant rates with $Fe(NS)_3$ (see above) and that the outcome of the experiments is not affected by 1 additional mol of **IIa**, eqn. (9). Combining these results with that of the previous section indicates

$$\mathbf{III}' + \mathbf{IIa} + M(NS)_2 \longrightarrow \mathbf{IIa} + N_4FeMX_4 + 3Cu(NS)(s) + Cu(NS)_2 \qquad (9)$$

that the selectivity order for transmetalation of **I** is **II** > **IIa** > $M(NS)_2$, (M = Co, Ni, Cu, Zn) under equimolar reaction conditions.

Simultaneous Transmetalation of I with Equimolar IIa, M(NS)₂, and M′(NS)₂ where M and M′ are the Same or Different Metals

We know from the previous section that treatment of **I** with equimolar **IIa** and $M(NS)_2$ proceeds via **III**′, eqn. (4). We verified that all the title reactions of this section can be run simultaneously without the necessity of preforming **III**′. It is also unnecessary to preform **III** in its corresponding reactions with $M(NS)_2$ reagents [4].

Intermediates **VII**, Scheme 1, do not accumulate in the reactions of **III** with 2 mol of $M(NS)_2$ evidently because the three copper centers are transmetalated at the same rate, eqn. (10) [9]. The corresponding reactions of **III**′ gave trimers **IX**′, eqn. (11) (Scheme 2), which were most often oxidized *in situ* with dioxygen to give trimers **X**′ (see below). Analytical data for an example of **IX**′ are given in Table 1.

$$\mathbf{III} + 2M(NS)_2 \longrightarrow \mathbf{IX} + 2Cu(NS)(s) + Cu(NS)_2 \qquad (10)$$

$$\mathbf{III}' + 2M(NS)_2 \longrightarrow \mathbf{IX}' + N + 2Cu(NS)(s) + Cu(NS)_2 \qquad (11)$$

Complexes **III** are selectively transmetalated to **VIII** by the less thermodynamically stable complex $M(NS)_2$ of an equimolar reactant mixture, eqn. (12), where M and M′ are different metals; this result is

$$\mathbf{III} + M(NS)_2 + M'(NS)_2 \xrightarrow{N} \mathbf{VIII} + M'(NS)_2 + Cu(NS)_2 + 2Cu(NS)(s) \qquad (12)$$

obtained because intramolecular NS ligand transfer in **VII** is faster than the transmetalation of its copper(II) center by $M'(NS)_2$ [4]. Establishment of M/M′ reactant selectivity is possible because $M'(NS)_2$ does not transmetalate the cobalt(II) centers of **VIII** on account of the stability order $Cu(NS)_2 > Ni(NS)_2 > Co(NS)_2$ and because $Co(NS)_2$ does not transmetalate M in products **VIII** [4].

When **IIIa**′ was treated with an equimolar mixture of $M(NS)_2$ and $M'(NS)_2$ we obtained dimers $N_4MM'Cl_4$ containing negligible iron (Table 2). This result is interpreted as follows, where $M(NS)_2$ is less thermodynamically stable than $M'(NS)_2$.

$$\mathbf{IIIa}' + M(NS)_2 \longrightarrow \mathbf{VIIa}' + 2Cu(NS)(s) \qquad (13)$$

$$\mathbf{VIIa}' \xrightarrow{N} N_4FeMCl_4 + Cu(NS)_2 \qquad (14)$$

$$N_4FeMCl_4 + M'(NS)_2 \longrightarrow N_4MM'Cl_4 + Fe(NS)_2 \qquad (15)$$

$$\text{net } \mathbf{IIIa}' + M(NS)_2 + M'(NS)_2 \longrightarrow N_4MM'Cl_4 + 2Cu(NS)(s) + Cu(NS)_2 + Fe(NS)_2 \qquad (16)$$

Negligible iron in the dimeric products indicates the stability order $Fe(NS)_2 > M(NS)_2$ for M = Co, Ni, Zn, which accounts for reactions (15).

Unfortunately, we found no way of separating $Fe(NS)_2$ from coproduct $Cu(NS)_2$ in net reaction (16) or of synthesizing it independently from $Fe(NS)_3$. The present stability order is thus $Cu(NS)_2 > (Fe(NS)_2, Fe(NS)_3) > Ni(NS)_2 > Co(NS)_2 > Co(NS)_3 > Zn(NS)_2$. This order predicts that copper(II) centers should be directly transmetalated by $Fe(NS)_2$, which we hope to confirm once this complex has been synthesized.

Air-sensitivity of Iron(II) Containing Products

Complexes **I**, **III** and **IX**, Scheme 1, are air-sensitive but they can be analyzed as solids under rigorously dioxygen-free conditions [3, 4]. We were not satisfied with most of the analytical or spectral

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*The product mixture was immediately separated to avoid complications from oxidation of excess **IIa**, eqn. (1).

data for solid dimers N_4FeMX_4 (eqn. (8)) or trimers $N_3M_2Fe(NS)_2X_4$ (eqn. (11)) isolated by adding the respective filtrates in nitrobenzene to excess deoxygenated hexane. The yields were low and Mössbauer spectroscopy showed clear evidence for contamination with iron(III). Manometric dioxygen uptake by the filtrates was consistent with eqns. (17) and (18). Our formulation of the iron(II) reactants is based on the corresponding cobalt(II) complexes, Scheme 1 [2–4] and data (Table 1) for one example of **IX**′.

$$4N_4MFe^{II}X_4 + O_2 \longrightarrow 2(N_4MFe^{III}X_4)_2O \qquad (17)$$

$$\mathbf{IX}' + 3O_2 \longrightarrow 2(N_3M_2Fe^{III}X_4O)_2 + 2N_2S_2 \qquad (18)$$

The formulation of the products of eqns. (17) and (18) also is speculative because the subsequent necessary separation* of the oxidized filtrates by gel permeation chromatography resulted in hydrolysis to give products **VIII**′ and X′, Scheme 2, presumably via eqns. (19) and (20), respectively.

$$(N_4MFe^{III}X_4)_2O + H_2O \longrightarrow \underset{\mathbf{VIII}'}{2N_4MFe(OH)X_4} \qquad (19)$$

$$(N_3M_2Fe^{III}X_4O)_2O + H_2O \longrightarrow \underset{\mathbf{X}'}{2N_3M_2Fe(OH)X_4O} \qquad (20)$$

By contrast, cobalt(II) dimers **VI** and **VIII**, Scheme 1, do not react at significant rates with dioxygen, which greatly simplifies their isolation and characterization [3, 4].

Dimers VIII′

Analytical data for dimers **VIII**′ obtained from eqns. (8) and (9) after oxidation, eqn. (17), and gel permeation chromatographic isolation, eqn. (19), are given in Tables 1 and 2. These new dimeric products contain Fe(OH) and M centers, where M is Co, Ni, Cu or Zn. Their room-temperature Mössbauer spectra exhibit isomer shifts 0.25 ± 0.03 mm/s and quadrupole splittings 0.55 ± 0.05 mm/s, consistent with the presence of iron(III) [17]. There was no systematic dependence of these parameters on the number of d-electrons in M. The sharp IR band expected for O–H stretching in Fe(OH) (see below) is obscured by broad absorption centered at 3400 cm^{-1} due to coordinated water in **VIII**′. A single, strong IR band at 1635 cm^{-1} indicates monodentate N in dimers **VIII**′ [2–10].

The electronic spectra of **VIII**′ in methylene chloride are shown in Fig. 3. The absorption of **VIIIb**′ (M = Ni) and **VIIId**′ (M = Zn) is largely due to their Fe(OH) centers, with $\epsilon \approx 80\ M^{-1}\ cm^{-1}$ at 680 nm, since Ni^{II} and Zn^{II} have negligible absorption in this region [2]. Product **VIIIa**′ exhibits clear spectral evidence for cobalt(II) at 610 nm [2–4]; however, ϵ_{610} is about two times larger than observed in N_4CoMCl_4 complexes **VIII** (Scheme 1; M = Co, Ni, Zn) [3, 4]. Strong absorption centered at 790 nm is due to copper(II) in product **VIIIc**′.

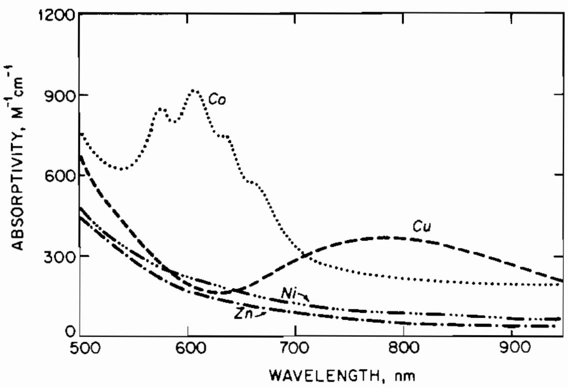

Fig. 3. Electronic spectra of dimers $N_4Fe(OH)CoCl_4{\cdot}H_2O$ (VIIIa′) (·······); $N_4Fe(OH)NiCl_4{\cdot}H_2O$ (VIIIb′) (– ··· –); $N_4Fe(OH)CuCl_4{\cdot}H_2O$ (VIIIc′) (– – –); and $N_4Fe(OH)ZnCl_4{\cdot}H_2O$ (VIIId′) (– · –) in methylene chloride at 25 °C.

Stoichiometry and Products of Oxidation of III′ by Dioxygen

Manometric dioxygen uptake experiments in nitrobenzene were consistent with overall reactions (21), which involve oxidation of two copper(I), two NS ligands and the formal iron(II) center of **III**′ by

$$4\mathbf{III}' + 5O_2 \longrightarrow 2(N_4Cu_3FeX_4O_2)_2O + 4N_2S_2 \qquad (21)$$

dioxygen: X and N are not oxidized, and neither is the cobalt(II) center of **III** [3, 4]. Uptake proceeded in two, well separated stages, the first of which has stoichiometry $\Delta(\mathbf{III}')/\Delta(O_2) = 1.0 \pm 0.1$; this incidates that the second stage is due to iron(II) oxidation [2, 3].

We have reported the kinetics of the four-electron reduction of dioxygen by excess **III** [3] (from eqn. (3)) and $N_3Cu_3M(NS)X_4$ [2] complexes (from eqn. (5)) in methylene chloride and nitrobenzene. These reactions result in substantial absorbance increases at 650–900 nm due to oxidation of copper(I) to copper(II) and are easily monitored by conventional spectrophotometry. The rate-determining step in all cases is insertion of dioxygen into the Cu_3MX_4 cores of these molecules [2, 3].

Attempts to replicate these measurements with excess **III**′ as the reductant were frustrated by very small absorbance changes at 650–900 nm, which led to very poor kinetic reproducibility. These difficulties are mainly due to the high absorption of iron(II) in excess **III**′ at 650–900 nm (Fig. 2) that precludes accurate kinetic measurements of the two stages

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*Gel permeation chromatographic product separation is necessary because of the presence of trace oxidized Cu(NS)(s) [2–4], $Cu(NS)_2$ and the disulfide N_2S_2 as coproducts.

of oxidation (see above) under conditions employed previously [2, 3].

Gel permeation chromatography separated trace oxidized Cu(NS)(s) (from eqn. (4)) and N_2S_2 (which was identified as before [2–4]) from **IV**′, the result of hydrolysis, eqn. (22), of the presumed first product of eqn. (21).

$$(N_4Cu_3FeX_4O_2)_2O + H_2O \longrightarrow 2IV' \qquad (22)$$

Analytical and cryoscopic data (Table 1) indicate that **IV**′ are unassociated tetramers in nitrobenzene. They differ from **IV** (Scheme 1) in having four coordinated N ligands. Their transmetalation behavior (see below) is consistent with the core structure in Scheme 2. All other known examples of this core structure (μ_4-O,μ-O)$N_nCu_3MX_4$, (M = Co, Ni, Cu, Zn) [2–4, 11] have n = 3, which indicates a high affinity of iron(II) (formally in **III**′) and iron(III) (in **IV**′) for N.

Spectral Properties of IV′

Room temperature Mössbauer spectra of **IVa**′ exhibited an isomer shift (0.31 ± 0.02 mm/s) and quadrupole splitting (0.79 ± 0.03 mm/s) expected for iron(III) [17]. Sharp, single bands at 3400 (νFeO–H) and 1635 cm^{-1} (monodentate N) [2–10] were observed in the IR spectra of **IV**′; negligible absorption at 1000 cm^{-1} confirmed the absence of coordinated NS^-, which is oxidized to non-coordinated disulfide N_2S_2 in eqn. (21).

The electronic spectra of **IV**′, Fig. 4, are dominated by two bands in the near-IR region that are very characteristic of copper(II) in this ligand system [2–10]. Average maximum absorptivities for (μ_4-O,μ-O)$N_3Cu_3M(H_2O)X_4$ complexes are 730 (X = Cl) and 1100 M^{-1} cm^{-1} (X = Br) [2]. The somewhat higher values for **IV**′, Fig. 4, are attributed to the presence of a metal(III) center, Fe(OH), in a common tetranuclear structure. A similar enhancement of cobalt(II) absorption by Fe(OH) in **VIIIa**′ was noted in an earlier section.

Transmetalation of IV′ *with M(NS)*$_2$ *Reagents*

Molecules **IV**′ react with 2 mol of $M(NS)_2$ reagents (M = Co, Ni, Cu) in methylene chloride or nitrobenzene to give trimers **X**′ (eqn. (23) and Scheme 2). Analytical, cryoscopic and spectral data for these products (Table 2) were indistinguishable from those for isolated products **X**′ of oxidation of **IX**′ with dioxygen, reactions (11), (18) and (20). Loss of 1 mol of CuO on transmetalation of (μ_4-O,μ-O)$N_3Cu_3M(OH_2)X_4$ molecules with 2 mol of $M(NS)_2$ reagents is apparently characteristic of this particular dioxometal core structure [2–4]. The one known exception to this type of CuO loss on transmetalation is for (μ_4-O,μ-O)$N_3Cu_3Cu(OH_2)Cl_4$, which is selectively transmetalated in stoichiometric steps by $Ni(NS)_2$ to give the family (μ_4-O,μ-O)$N_mCu_{4-x}Ni_xCl_4$, all members of which have been spectrally identified [11].

$$IV' + 2M(NS)_2 \longrightarrow X' + N \cdot CuO + 2Cu(NS)_2 \qquad (23)$$

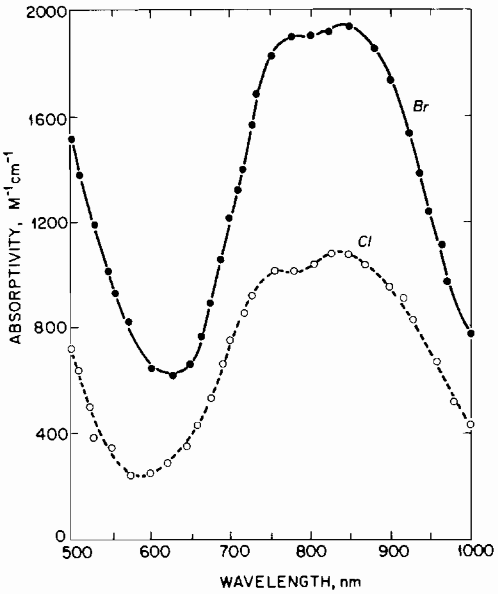

Fig. 4. Electronic spectra of $N_4Cu_3Fe(OH)X_4O_2$ complexes **IVa**′ (○) and **IVb**′ (●) (Table 1) in methylene chloride at 25 °C.

Trimers X′

The room temperature Mössbauer spectrum of trimer $N_3Ni_2Fe(OH)Cl_4O$ has the isomer shift (0.29 ± 0.02 mm/s) and quadrupole splitting (0.81 ± 0.03 mm/s) expected of an iron(II) complex [17]. The sharp bands at 3400 and 1635 cm^{-1} in the IR spectra of solids **X**′ are assigned to ν(FeO–H) and monodentate N, respectively. The electronic spectra of X′ (M = Co, Ni, Zn), Fig. 5, are similar to those for **VIII**′, Fig. 3. No features are observed with M = Ni and Zn and the absorptivities of M and Fe(OH) are low. Unusually strong absorption (ϵ_{610} = 1400 M^{-1} cm^{-1}) due to cobalt(II) in $N_3Co_2Fe(OH)Cl_4O$ is attributed to the presence of its iron(III) center: for comparison, (μ_3-O)$N_3Co_2ZnCl_4 \cdot 3H_2O$ has ϵ_{610} = 670 M^{-1} cm^{-1} in methylene chloride [4].

Transmetalation of IV′ *with IIa*

In previous work we found that cobalt(III) complex **II** is an excellent transmetalator of copper(II) centers because of its low relative thermodynamic stability [3, 4]. However, the Co^{III}(NS) centers introduced by transmetalation spontaneously self-destruct, eqns. (24)–(26), with the result that all the products contain cobalt(II). We have noted that $Fe(NS)_3$ (**IIa**) is air-sensitive in solution, eqn. (1), while $Co(NS)_3$ (**II**) can be crystallized intact [21d]. Also, only one iron center can be introduced by

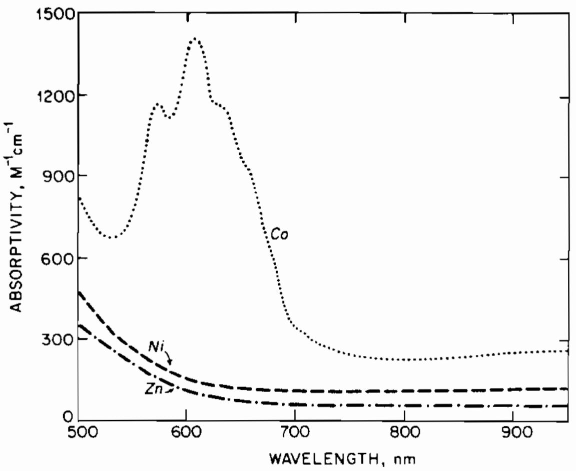

Fig. 5. Electronic spectra of trimers $N_3Fe(OH)Co_2Cl_4O$ (Xa′) (·······); $N_3Fe(OH)Ni_2Cl_4O$ (Xb′) (– – –); and $N_3Fe(OH)Zn_2Cl_4O$ (Xd′) (– · –) in methylene chloride at 25 °C.

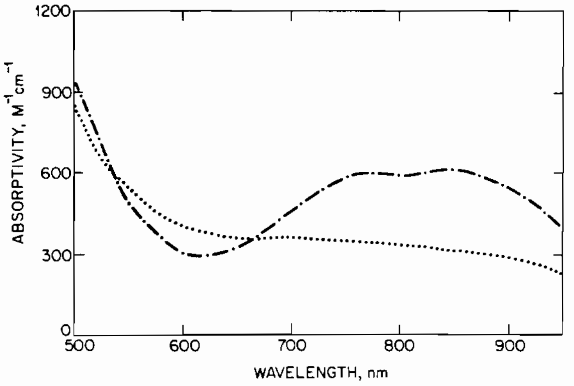

Fig. 6. Electronic spectra of trimers $N_3Fe(OH)Cu_2Cl_4O$ (Xc′) (– · –) and $N_3Fe(OH)CuFe(NS)Cl_4O$ (XI′) (·······) in methylene chloride at 25 °C.

$$\equiv Cu^{II} + \mathbf{II} \longrightarrow \equiv Co^{III}(NS) + Cu(NS)_2 \tag{24}$$

$$\equiv Co^{III}(NS) \longrightarrow \equiv Co^{II} + NS^{\bullet} \tag{25}$$

$$2NS^{\bullet} \longrightarrow N_2S_2 \tag{26}$$

transmetalation of **I** with **IIa** to give **III′**. It was therefore of considerable interest to see if dioxocopper(II) tetramers **IV′** reacted with **IIa**, and whether or not the resulting Fe(NS) centers self-destruct.

We are pleased to report that **IV′** can be transmetalated with 1 or 2 mol of **IIa**, respectively, eqns. (27) and (28) (Scheme 2). Loss of CuO was observed

$$\mathbf{IV'} + \mathbf{IIa} \longrightarrow \mathbf{XI'} + N^{\bullet}CuO + Cu(NS)_2 \tag{27}$$

$$\mathbf{IV'} + 2\mathbf{IIa} \longrightarrow \mathbf{XII'} + N^{\bullet}CuO + 2Cu(NS)_2 \tag{28}$$

as in eqn. (23). Reactions (27) and (28) are much slower than the corresponding reactions of **II** and required 24 and 36 h for completion, respectively, under typical [3, 4] experimental conditions. Complicated product mixtures resulted if the reactions were not run in the rigorous absence of dioxygen and water because of eqn. (1) and hydrolysis [23]. Elemental analyses (Table 2) reveal that isolated products $(\mu_3\text{-}O)N_3CuFe(OH)Fe(NS)Cl_4$ (**XI′**) and $(\mu_3\text{-}O)N_3Fe(OH)(Fe(NS))_2Cl_4$ (**XII′**) contain one and two coordinated NS ligands, respectively, indicating that their Fe(NS) do not self-destruct*. The analytical data (Table 2) indicate that **XI′** is much more stable than cobalt(II) analogues **XI**, Scheme 1, which disproportionate to give CuO during transmetalation [3].

Isolated solid **XII′** is very insoluble in nitrobenzene or methylene chloride, presumably because of extensive intermolecular bonding through monodentate NS ligands. The mull electronic spectrum of this solid exhibited strong absorption in the 550–750 nm region which we attribute to its two Fe(NS) centers. The IR spectra of solids **XI′** and **XII′** exhibited bands at 1635 cm^{-1} (monodentate N) and at 1000 cm^{-1} due to coordinated NS [2–4]. However, the latter were broader and weaker than for bidentate NS in $M(NS)_n$ complexes [18–21], which leads to the tentative formulations of **XI′** and **XII′** containing six-coordinate iron(III) in Scheme 2.

By contrast, solid $(\mu_3\text{-}O)N_3CuFe(OH)Fe(NS)Cl_4$ (**XI′**) is sufficiently soluble in aprotic solvents to permit reliable cryoscopic and spectral measurements. The cryoscopic data (Table 2) indicate that **XI′** is an unassociated trimer in nitrobenzene. The electronic spectra of trimers **Xc′** and **IX′** are compared in Fig. 6. The absorptivity of **XI′** at 850 nm is about half that of **Xc′**, which contains two copper(II) centers and Fe(OH). We feel that the Fe(NS) center of **XI′** is responsible for the lack of a minimum at *c.* 600 nm in its electronic spectrum. This absorption is in the region expected for $Fe^{III}(NS)_n$ centers, as seen in the spectrum of **IIa**, Fig. 1.

Our observation of stable Fe(NS) groups in transmetalated products suggests that other copper(II) complexes can be transmetalated with **IIa** with the same result. We are exploring this possibility and the catalytic properties of iron–copper complexes. The results will be reported in future papers.

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*The stability of product Fe(NS) centers is indicated by analytical data for isolated products XI′ and XII′ (Table 2).

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