Binuclear and Trinuclear Nitrato-complexes of Copper(II) and Nickel(II) with Bidentate Schiff Bases

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The reaction of copper(II) and nickel(II) *N*-alkylsalicylaldimine complexes with copper(II) and nickel(II) nitrate respectively, results in a series of binuclear copper(II) and trinuclear nickel(II) complexes. The copper complexes exhibit strong pairwise antiferromagnetic interactions and are assigned an approximately planar structure with co-ordinated nitrato-groups. The nickel complexes show no strong exchange interactions, but they appear to be weakly ferromagnetic. The proposed structure for these complexes contains a central octahedral nickel bonded to two nitrato-groups and two pseudo-tetrahedral nickel atoms. The nitrato-group behaves like a halogen in the copper complexes, but there is no halogen analogue of the nickel complexes.

BINUCLEAR and trinuclear complexes of copper(II) with Schiff base ligands are readily formed by reacting monomeric copper Schiff base complexes (CuL or CuL_2) with copper(II) salts CuX_2.[1] Binuclear complexes have been isolated in cases where X is a good donor atom (Cl or Br) and L a bidentate or tetradentate ligand,[2,3] and trinuclear complexes were obtained when X is anionic and L tetradentate.[4] The postulated structures of some of these complexes were subsequently confirmed by single-crystal *X*-ray studies.[5-8]

The properties of nickel(II) Schiff base complexes sometimes resemble those of their copper(II) analogues.[9] Thus nickel(II) analogues of the bi- and tri-nuclear copper(II) complexes with tetradentate L are readily formed, but for bidentate L, nickel analogues of the binuclear $[CuLX]_2$ (X = Cl or Br) have not been isolated in the solid state.[4]

Here we examine and compare the products of the reaction of bidentate copper(II) and nickel(II) Schiff base complexes with the metal nitrates.

EXPERIMENTAL

The monomeric copper(II) and nickel(II) salicylaldimine complexes were prepared by literature methods.[9]

Nitrato(N-*methylsalicylaldiminato*)*copper*(II) *Monohydrate.*—Bis(*N*-methylsalicylaldiminato)copper(II) (4 g) dissolved in a minimum of methanol was reacted with a slight excess of copper(II) nitrate pentahydrate (3 g) in methanol (40 ml) and the volume of the resulting solution reduced slightly using a rotary evaporator. Small green crystals formed after one day (Found: C, 36·1; H, 3·4; N, 10·2. $C_{16}H_{18}Cu_2N_4O_9$ requires C, 35·8; H, 3·4; N, 10·4%).

Nitrato(N-*methylsalicylaldiminato*)*copper*(II).— Bis(*N*-methylsalicylaldiminato)copper(II) (5 g) in chloroform (100 ml) was added to copper(II) nitrate pentahydrate (2 g) in ethanol (20 ml) and the volume reduced to 50 ml. The product formed as fine green crystals (Found: C, 36·8; H, 3·1; N, 10·4. $C_{16}H_{16}Cu_2N_4O_8$ requires C, 37·0; H, 3·1; N, 10·8%).

Nitrato(N-*ethylsalicylaldiminato*)*copper*(II).— Bis(*N*-ethylsalicylaldiminato)copper(II) (5·5 g) in a minimum of methanol was mixed with a slight excess of copper(II) nitrate pentahydrate (4 g) in methanol (50 ml) and the solution was allowed to stand overnight. The volume of the resulting solution was then reduced to *ca.* 50 ml using a rotary evaporator and after a few days the product formed as a dark green crystalline material (Found: C, 39·3; H, 3·8; N, 9·9. $C_{18}H_{20}Cu_2N_4O_8$ requires C, 39·5; H, 3·7; N, 10·2%).

Nitrato(N-*n-propylsalicylaldiminato*)*copper*(II) *Monohydrate.*—The above reaction was repeated using bis(*N*-n-propylsalicylaldiminato)copper(II) (6·4 g) and copper(II) nitrate pentahydrate (3·9 g). The product formed as a green powder after several hours (Found: C, 40·4; H, 4·5; N, 8·9. $C_{20}H_{26}Cu_2N_4O_9$ requires C, 40·5; H, 4·4; N, 9·4%).

Nitrato(N-*iso-butylsalicylaldiminato*)*copper*(II) *Monohydrate.*—The above reaction was repeated using bis(*N*-isobutylsalicylaldiminato)copper(II) (7 g) and copper(II) nitrate pentahydrate (4·6 g). The fine green crystalline product formed immediately (Found: C, 42·7; H, 5·1; N, 8·7. $C_{22}H_{30}Cu_2N_4O_9$ requires C, 42·5; H, 4·9; N, 9·0%).

Nitrato(N-*methyl-3-methoxysalicylaldiminato*)*copper*(II) *Monohydrate.*—The above reaction was repeated using bis(*N*-methyl-3-methoxysalicylaldiminato)copper(II) (6 g) and copper nitrate (4 g). The green crystalline product formed after several days (Found: C, 36·2; H, 4·1; N, 8·7. $C_{18}H_{22}Cu_2O_{11}N_4$ requires C, 36·2; H, 3·9; N, 9·3%).

Nitrato(N-*cyclohexylsalicylaldiminato*)*copper*(II) *Monohydrate.*—Bis(*N*-cyclohexylsalicylaldiminato)copper(II) (6 g) was warmed in methanol (200 ml) and small portions of chloroform were added to aid dissolution. Copper(II) nitrate pentahydrate (3·6 g) in methanol (50 ml) was added and the volume of this solution reduced to *ca.* 100 ml using a rotary evaporator. The product formed almost immediately as a green powder (Found: C, 46·3; H, 5·3; N, 7·8. $C_{26}H_{34}Cu_2N_4O_9$ requires C, 46·3; H, 5·1; N, 8·3%).

Nitrato(N-*benzylsalicylaldiminato*)*copper*(II).— Bis(*N*-benzylsalicylaldiminato)copper(II) (3·5 g) was heated in methanol–chloroform (1 : 1) and then added to a solution of copper(II) nitrate pentahydrate (2·1 g) in methanol (40 ml). After heating for an hour the solution was allowed to stand

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for a few days during which time the powdery green-brown product formed (Found: C, 50·1; H, 3·7; N, 8·1. $C_{28}H_{24}Cu_2N_4O_8$ requires C, 50·1; H, 3·6; N, 8·3%).

Nitrato(N-*methyl-5-chlorosalicylaldiminato*)*copper*(II).—The above reaction was repeated using bis(*N*-methyl-5-chlorosalicylaldiminato)copper(II) (4·5 g) and copper(II) nitrate pentahydrate (3·2 g). The product formed as a light green powder (Found: C, 32·8; H, 2·4; N, 9·3. $C_{16}H_{14}Cu_2Cl_2N_4O_8$ requires C, 32·7; H, 2·4; N, 9·5%).

Dinitrato[*bis*(*bis*(N-*ethylsalicylaldiminato*)*nickel*(II))]*nickel*(II).—Bis(*N*-ethylsalicylaldiminato)nickel(II) (3·5 g) was dissolved in a minimum of methanol–chloroform (1 : 1) and then added to nickel(II) nitrate hexahydrate (1·5 g) in methanol (40 ml). The resulting solution was heated for an hour and left to stand for two weeks. The product formed as large pale green crystals (Found: C, 48·4; H, 4·5; N, 9·5. $C_{36}H_{40}Ni_3N_6O_{10}$ requires C, 48·3; H, 4·5; N, 9·4%).

		Melting point (°C)			Selected infrared bands (cm^{-1})				Equation (1)		E.s.r.		
R	R′	CuL	$CuL_2,Cu(NO_3)_2$	λ/cm^{-1}			$-ONO_2$ bands	H_2O band	$-J$/cm^{-1}	g	$g_{\parallel}$	$g_{\perp}$	g
Copper complexes													
Me	H	155	192	15,000	1270	1565(22)[a]	811sh, 1019s, 1286s, 1492sh		280	2·12	2·29	2·026	2·12
Me	H *		188		1270	1566(22)	810sh, 1019s, 1286s, 1492sh	3400					
Et	H	146	187	15,200	1267	1558(17)	803m, 1018s, 1285s, 1495w		83	2·14	2·35	2·058	2·16
$(CH)_2CH_3$	H *	126	167	15,000	1267	1562(20)	807w, 1028m, 1282s	3400	350	2·20	2·32	2·018	2·12
$CH_2CH(CH_3)_2$	H *	148	Decomp.	14,800, 12,400	1263	1565(21)	809w, 1028s, 1281s, 1495sh	3400	191	2·18	2·32	2·002	2·11
cyclohexane	H *	176	190	13,500, 11,000	1268	1558(16)	807m, 1004s, 1284s, 1492sh	3400	208	2·12	2·30	2·045	2·13
$CH_2{\cdot}C_6H_5$	H	187	180	15,700	1265	1558(20)	781m, 1007s, 1218s, 1503sh		120	2·08	2·22	2·037	2·10
Me	5-Cl	236	212	14,800	1268	1561(20)	805m, 1010s, 1280s, 1495sh		136	2·21			
Me	3-OMe *				1270s	1563(22)	810m, 1015m, 1288s, 1498sh	3400	43	2·17			
		λ/cm^{-1}, $(NiL_2)_2,Ni(NO_3)_2$											
Nickel complexes													
Et	H	25,000—35,000(vs), 15,300, 8500—9000, 6800(w)			1270	1568(24)	806, 1020, 1290, 1505sh						
$CH(CH_3)_2$	H *	25,000—35,000(vs), 15,100, 800—9000, 6900(w)			1270	1567(23)	805, 1020, 1290, 1505sh	3450					

* Hydrate.

[a] Shift with respect to CuL_2 or NiL_2 in parentheses.

Dinitrato[*bis*(*bis*(N-*iso-propylsalicylaldiminato*)*nickel*(II))] *nickel*(II) *Dihydrate*.—The above preparation was repeated using bis(*N*-isopropylsalicylaldiminato)nickel(II) (3·8 g). The product formed as a light green powder (Found: C, 49·2; H, 5·0; N, 8·6. $C_{40}H_{48}Ni_3N_6O_{10}$ requires C, 49·0; H, 4·9; N, 8·6%).

Infrared spectra were determined on Nujol and hexachlorobutadiene mulls of the compounds using a Unicam SP 200 and a Perkin-Elmer 221 spectrophotometer. The spectrum of a polystyrene film was recorded on the same chart as a reference to allow accurate measurements of the bands. Electronic spectra were determined on the solid compounds using a Unicam SP 700 spectrophotometer. E.s.r. measurements were made at 300 and 77 K on a Varian V4502-15 spectrometer at the Physics and Engineering Laboratory of the D.S.I.R., Wellington. Magnetic susceptibility measurements were made by the Gouy method [3,4] in the range 77—400 K. Measurements below 77 K were made using a Foner balance.[10] Diamagnetic corrections were calculated from Pascal's constants.

RESULTS AND DISCUSSION

Synthesis.—In the case of copper(II), only 1:1 adducts of the type $CuL_2,Cu(NO_3)_2$ could be prepared by the direct reactions described, and with nickel(II), only 1 : 2 adducts of the type $(NiL_2)_2,Ni(NO_3)_2$ were formed. When the reagents were mixed in proportions different to those described above, the same complexes formed in smaller yields, but no other compounds were isolated. In many cases the solid product crystallised only slowly from solution, although rapid and dramatic colour changes, especially with the nickel complexes, indicated that a reaction occurs and goes to completion in the first few seconds after mixing the reagents. Possibly, the rate-determining step is the co-ordination of nitrate groups to bi- or tri-nuclear solution species.

Electronic Spectra.—The absorption bands of copper compounds (Table) in the visible region closely resemble those of the binuclear complexes (**1**; X = Cl or Br), in good agreement with a four-co-ordinated distorted planar environment about the copper atoms.[1,2,4,11]

The spectra of the nickel complexes are quite different from those of the parent monomeric salicylaldimines NiL_2, in which the metal environment is intermediate between planar and tetrahedral, and closer to tetrahedral in the isopropyl than the ethyl complex.[11,12]

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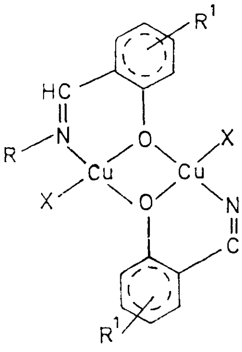
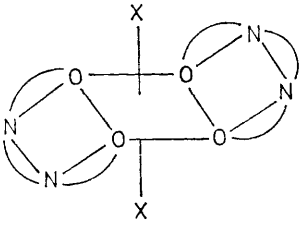
The spectra of the $(NiL_2)_2,Ni(NO_3)_2$ complexes are in better accord with octahedral nickel(II) environments, so that the bands *ca.* 9000 and 15,000 cm^{-1} may be assigned to the $^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ transitions respectively.[13] The broad band at 25,000—35,000 cm^{-1} may contain the $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transition, but the high intensity of these bands suggests that their origin is mainly charge-transfer. The bands *ca.* 7000 cm^{-1} are characteristic of nickel(II) in pseudo-tetrahedral salicylaldimine complexes and are not likely to arise from octahedral nickel(II).[9] Other bands due to tetrahedral sites are probably obscured by the other, relatively stronger, absorptions. Thus, it is likely that the complexes contain nickel in both octahedral and tetrahedral environments.

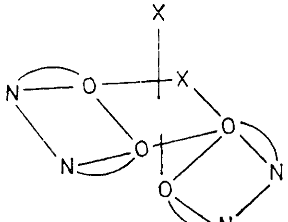
Infrared Spectra.—The formation of bi- and tri-nuclear complexes such as (1)—(3) from the monomeric parent complexes, results in specific changes in the i.r. spectrum: a shift (*ca.* 20 cm^{-1}) to higher frequencies of the band *ca.* 1540 cm^{-1}, smaller shifts (5—10 cm^{-1}) to higher frequencies in the bands *ca.* 760, 1140, 1480, and 1620 cm^{-1}, shifts to lower frequencies of the band *ca.* 910 cm^{-1}, the appearance of new bands *ca.* 1150, 1210, and 1270 cm^{-1}, and the disappearance of the bands *ca.* 970 and 1190 cm^{-1}.[1-4] The formation of $CuL_2,Cu(NO_3)_2$ and $(NiL_2)_2,Ni(NO_3)_2$ from CuL_2 and NiL_2 results in the same changes in i.r. spectra, except that no band appeared at 1210 cm^{-1}. Thus the phenolic oxygen bridging observed in (1) and (2) must also exist in the $CuL_2,Cu(NO_3)_2$ and $(NiL_2)_2,Ni(NO_3)_2$. The absorptions in these complexes *ca.* 806, 1020, 1290, and 1505 cm^{-1} which are absent in CuL_2, NiL_2, or (1; X = Cl or Br) indicate that the nitrate groups are co-ordinated.[14] The hydrated complexes $CuL_2,Cu(NO_3)_2,H_2O$ and $(NiL_2)_2,Ni(NO_3)_2,2H_2O$ [R = $CH(CH_3)_2$] also exhibit broad bands *ca.* 3400 cm^{-1}, although these could not be used to determine whether the water was co-ordinated or not. However, the hydrated complexes did not show any other differences from the anhydrous complexes, so that aquo-co-ordination does not seem very likely.



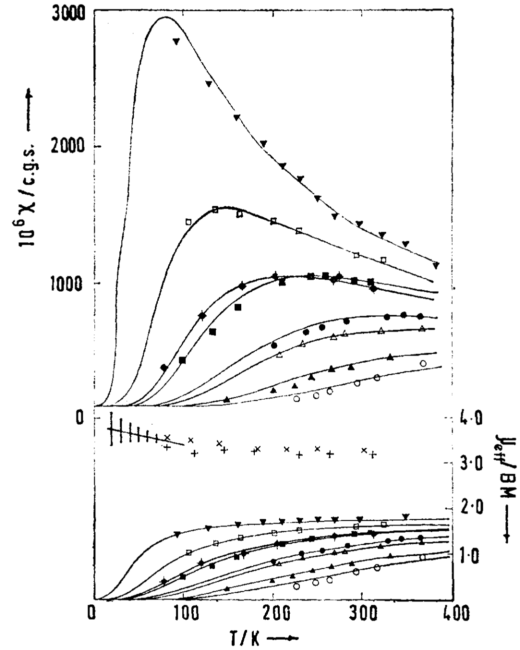
(1)



(2)



(3)



Magnetic moments and susceptibilities. The solid curves are calculated from equation (1) (*J* and *g* from the Table). The experimental points are $CuL_2,Cu(NO_3)_2$ with

▼ R = Me, R′ = 3-OMe
□ R = Et, R′ = H
◆ R = $CH_2{\cdot}C_6H_5$, R′ = H
■ R = Me, R′ = 5-Cl
● R = $CH_2{\cdot}CH(CH_3)_2$, R′ = H
△ R = cyclohexane, R′ = H
▲ R = Me, R′ = H
○ R = $(CH_2)_2CH_3$, R′ = H

and $(NiL_2)_2,Ni(NO_3)_2$

× R = Et
+ R = $CH(CH_3)_2$

Lower-temperature measurements on the last mentioned complex are shown as a solid curve with error bars arising from temperature uncertainty

Magnetism.—The magnetic properties of the copper complexes (Figure) conform well to the Bleaney–Bowers equation [15]

$$\chi_M = \frac{Ng^2\beta^2}{3kT}\left(1 + \tfrac{1}{3}e^{-2J/kT}\right)^{-1} + N\alpha \qquad (1)$$

where the symbols have their usual meanings.

A binuclear structure of type (1; X = $-O-NO_2$) is therefore indicated for these complexes. Only one of the complexes [$CuL_2,Cu(NO_3)_2$ R = Me and R′ = 3-OMe] is anomalous in that it exhibits a relatively small degree

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of antiferromagnetic interaction over the available temperature range. However, the similarity of its properties to those of the other complexes suggests a similar structure for this complex also.

The J values required to fit equation (1) (Table) are of the same order, but slightly lower, than for the analogues with X = Cl. The magnetic properties of the analogous complexes with X = Br are also very similar.[2,3] This suggests that the basic skeleton of the complex (1) determines the antiferromagnetism, but alteration of the outside group X has no large consistent effect. The reversal of the J values for R = Me and R = Et in going from X = Cl to X = ONO_2 is interesting: this may well be due to differences in the degree of distortion from planarity of the environments of the two copper atoms. Single-crystal structural determinations show that small distortions of this type, with no change in bond lengths or the kind of bonds, significantly change the J values in complexes of type (1).[8]

Fitting of data to equation (1) is expected to yield good values of J but g values so obtained should be of much lower accuracy than obtainable from e.s.r. data.[16] E.s.r. spectra could be obtained for all the nitrato-complexes. The spectra were generally much better resolved at low temperature, where the increased population of the singlet state has the effect of magnetic dilution of the remaining triplet species.

The nickel complexes $(NiL_2)_2,Ni(NO_3)_2$ have all three nickel atoms paramagnetic. When R = Et, this implies a significant change in stereochemistry in the formation of the paramagnetic $(NiL_2)_2,Ni(NO_3)_2$ from the diamagnetic NiL_2. When R = $CH(CH_3)_2$ the nickel atoms are paramagnetic in both NiL_2 and $(NiL_2)_2,Ni(NO_3)_2$. The magnetic moments of the complexes rise steadily with decreasing temperature (Figure) suggesting the presence of nickel atoms sufficiently close to each other to permit ferromagnetic interactions, similar to those observed in the trinuclear nickel(II) acetylacetonate.[17]

A trinuclear structure of type (2), or possibly (3) (X = ONO_2) containing an octahedral and two pseudo-tetrahedral nickel atoms would best explain the experimental results for the $(NiL_2)_2,Ni(NO_3)_2$ complexes. The magnetic properties in either case would be described by equation (2), where $A = \exp(2J/kT)$, $B = \exp(2J'/kT)$,

$$\mu^2_{\mathrm{eff}} = \tfrac{1}{18} \cdot \frac{36f^2A^3 + 9(g+f)^2(1+5A^2)A^2B + 9(3g-f)^2B^3 + 5(5g+f)^2A^2B^3 + 56(g+2f)^2A^5B^3}{AB + 3(A^3 + A^2B + B^3) + 5A^2B(A^2+B^2) + 7A^5B^3} \qquad (2)$$

J and J' are the exchange integrals between adjacent and between extreme nickels respectively, and the g values for the extreme and the central atoms are designated as g and f respectively. If the complexes contain highly distorted tetrahedral nickels, μ(tet.) would be roughly constant and equation (2) would be valid, but if distortion is low, tetrahedral nickel atoms would, in isolation, have moments passing through a maximum at high temperatures and decreasing to a low value at very low temperatures.[18] This effect might be masked by the ferromagnetic interactions, but it could make equation (2) quite approximate.

The value of J' is expected to be much smaller than that of J.[4,17] Because of this, as well as the limitation of experimental accuracy and the limited diagnostic value of magnetic moments for ferromagnetic interactions, we assume $J' = 0$, $g = g'$. We then have $J \gtrsim 15$ cm^{-1} for each of the two complexes.

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