Novel Nickel(II) Dimers

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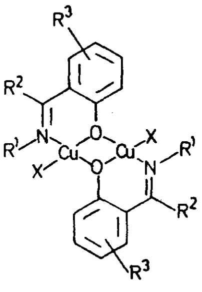
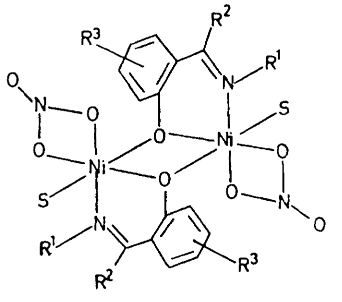
Summary Syntheses of nickel dimers derived from bidentate Schiff bases (bsb) and nitrato ligands, analogous to [Cu(bsb)halide]$_2$ dimers, are reported for the first time and their structures and magnetism compared with [Cu(bsb)NO$_3$]$_2$, whose structure is also reported.

COPPER(II) dimers (I) with bidentate Schiff base ligands, acting *trans* to each other are well-known,[1-5] and analogous nickel(II) complexes have long been sought. Trinuclear nickel complexes with such ligands have been prepared[2,6] but these are not of the same type as (I), and no dimeric compounds have so far been reported. The main difficulty in synthesis appears to have been interference of water molecules which compete with the other ligands. Binuclear nitrato complexes (II) have now been obtained in crystalline form from Ni(bsb)$_2$ and Ni(NO$_3$)$_2$·6H$_2$O in triethoxymethane which removes the water introduced by the hydrated nickel nitrate, producing ethanol.



(I)



(II)

TABLE
Crystallographic data

	(IIa)	(IIb)	(IIc)	(Ia)
a/Å	8·967(7)	8·833(8)	9·191(9)	9·678(6)
b/Å	9·601(3)	8·957(7)	8·964(9)	9·82(1)
c/Å	11·926(7)	11·81(1)	24·40(1)	16·267(7)
α/°	100·32(5)	100·74(6)	90	90
β/°	98·12(7)	92·08(8)	98·44(9)	134·69(4)
γ/°	114·01(3)	101·51(7)	90	90
V/Å^3	896	850	1988	1100
Space group ..	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	1	1	2	2
No. of reflections	2090	692		1425
R	0·029	0·129		0·038
Max. M–O distance/Å ..	2·185	2·21		2·148[a]
Min. M–O distance/Å ..	1·973	1·9		1·926

[a] 0·50 Å longer than the other metal–ligand bonds.

Single crystal X-ray diffraction studies have been carried out on two complexes; (IIa), R^1 = Me, R^2 = Ph, R^3 = 5-Cl, S = EtOH, and (IIb), R^1 = CHMe$_2$, R^2 = H, R^3 = 5,6-benzo, S = EtOH, and binuclear six-co-ordinated structures (*e.g.* Figure 1) were observed. Cell parameters, determined for two further complexes (IIc), R^1 = Et, R^2 = Ph, R^3 = 5-Cl, S = EtOH, and (IId), R^1 = Me, R^2 = Ph, R^3 = 5-Cl, S = PhN, are compatible with a similar structure. The structure of the analogous copper(II) complex, (Ia), R^1 = Et, R^2 = H, X = ONO$_2$, R^3 = H, prepared similarly to (IIa) and (IIb), was also determined (Figure 2). Crystal data are given in the Table. Once formed, both the nickel and copper complexes are relatively stable to moist air, and no decomposition occurred during the time of the X-ray data collection when the crystals were left exposed to the atmosphere. The complexes decompose slowly on immersion in water.

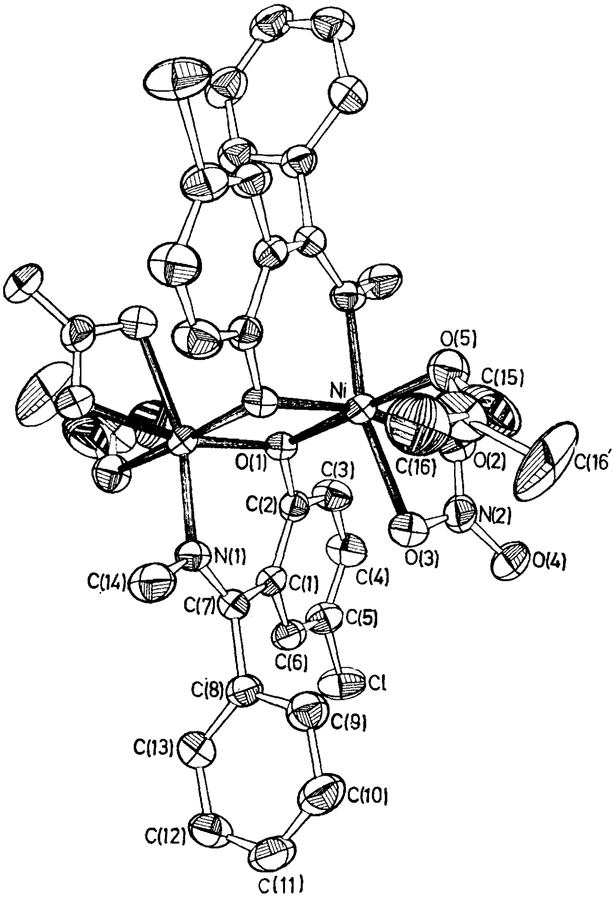


FIGURE 1. Molecular Structure of (IIa)

The main differences between (Ia) and type (II) complexes are the co-ordinated solvent in (II), and the weak fifth bond in (I) compared with the six nearly equal bonds in (II), distorted from O_h mainly by the narrow bite angles of the nitrato ligand and of the Ni$_2$O$_2$ bridge. The i.r. band near 1540 cm^{-1} shows a 15—20 cm^{-1} energy increase in (I) and (II) over Nibsb$_2$, Cubsb, supporting the assignment of these bands to the phenolic C–O stretch.[1,2,5]

The magnetic properties correlate with the structures; (Ia) shows antiferromagnetic interactions of magnitude compatible with the degree of distortion from planar towards tetrahedral geometry observed in several dimers such as (I) complexes,[1,3–5,7] if the weak fifth bond of (Ia) is ignored. By contrast, the ferromagnetism of the nickel dimers is only observable below liquid nitrogen temperatures and (IIa) is typical, the moment increases steadily from 3·1 BM at 100 K to a maximum of 4·0 BM at 7 K before decreasing sharply to 3·8 BM at 5 K, implying an intermolecular anti-ferromagnetic interaction superimposed on the pair-wise ferromagnetism. This inter-dimer interaction presumably occurs principally in the *a* direction along which each dimer is linked to its neighbour *via* two hydrogen bonds (EtO-H . . . . . ONO_2) to form a linear polymeric chain. Magnetic interaction can then occur *via* unpaired spin delocalisation on the ligands, a phenomenon demonstrated in systems with analogous A ground states.[8] The high temperature limit of the moment yields a reasonable g value of 2·2. To measure the inter-dimer interaction directly, type (II) complexes have been synthesised with S a non-hydrogen bonding ligand of varying bulkiness such as pyridine and triphenylphosphine oxide, and their structures will also be investigated.

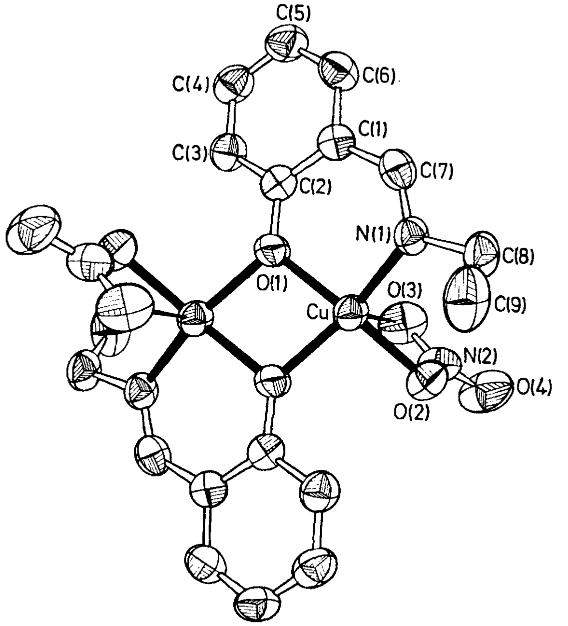


FIGURE 2. Molecular structure of (Ia)

$[NiX(bsb)S_n]_2$ form readily in solution for X = Cl, Br, but are not readily isolated in the solid, presumably because these complexes must bond to two solvent molecules per metal atom to attain octahedral Ni^{II}, while the type (II) nitrates need only one solvent molecule which may then be held by both co-ordination and hydrogen bonding if S is EtOH. Complex (IId) is unstable to loss of pyridine in the open, possibly due to the lack of hydrogen bonding to retain it; (IIc) is unstable to loss of EtOH, possibly indicating that some slight packing difference [compared to the analogous (IIa)] also prevents hydrogen bonding.

The structural elucidation of these nickel dimers, (II), opens up a new area of nickel(II) chemistry; as wide a range of type (II) complexes, as the well established type (I)[1–5] and its analogues[7] form under suitable conditions. A series of such nickel(II) complexes has been prepared, and comparison of electronic and i.r. spectra with those of (IIa), (IIb) and (IIc), establishes their dimeric octahedral structure. These and other related complexes are now under investigation.

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