The Electrochemical Properties and Crystal Structures of Some Nickel Diketone Bisthiosemicarbazones

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Summary The values of the reduction potentials of a series of nickel diketone bisthiosemicarbazones are shown to depend on the ligand substituents and on the extent of conjugation within the ligand framework: the structures of two complexes containing a seven-membered chelate ring have been determined by *X*-ray techniques.

NICKEL complexes containing *o*-mercaptoaniline, *e.g.* $[\mathrm{Ni}\{\mathrm{S(NH)C_6H_4}\}_2]^0$, thiobenzoylhydrazine, *e.g.* $[\mathrm{Ni}\{\mathrm{SC(PH)NNH}\}_2]^0$, and the related glyoxal bis(2-mercaptoanil) and biacetyl bis(thiobenzoylhydrazine) (I; R^1 = Ph, R^2 = R^3 = Me) undergo electron transfer reactions[1] similar to those of nickel bis-1,2-dithiolenes.[2] The complexes contain a basic $\mathrm{NiN_2S_2}$ co-ordination unit but differ principally in that the first two have two separate, bidentate, ligands whereas the last two contain fully-conjugated, tetradentate, tricyclic ligand systems. The influence of ligand substituents and of conjugation on the half-wave potentials of the one-electron transfer reactions which these complexes undergo are not known. Accordingly, we have prepared a series of nickel complexes derived from ketoaldehyde or diketone bis(thiosemicarbazones), which are related to nickel biacetylbis(thiobenzoylhydrazone), and have studied these by polarography and cyclic voltammetry.

The thiosemicarbazone complexes, (I), (II), (III), and (IV), were diamagnetic† in the solid state and in solution, even in strongly co-ordinating solvents such as pyridine and *NN*-dimethylformamide (DMF). In DMF, the complexes exhibited an ill-defined voltammetric oxidation wave (multi-electron process) beginning at *ca.* +1·00 v, and two reversible polarographic reduction waves. The electrochemical data (Table) show that the $E_{\frac{1}{2}}$-values depend on (a) the substituents on the azomethine bridge (a linear correlation of $E_{\frac{1}{2}}$ with Taft's σ^* inductive constant[3] can be made), (b) the substituents on the NNCS ring-fragments [*cf.* $E_{\frac{1}{2}}$-values of (I; R^1 = NHMe, R^2 = R^3 = Me) and (I; R^1 = Ph, R^2 = R^3 = Me)], and (c) the extent of conjugation around the ligand framework [*cf.* (II) with (I), (III) or (IV) or $[\mathrm{Ni}\{\mathrm{SC(Ph)NNH}\}_2]^0$ with (I; R^1 = Ph, R^2 = R^3 = Me)].

A comparison of the data obtained from (II) with those

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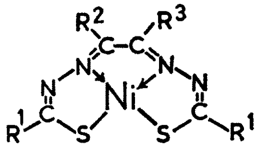
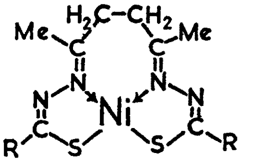
† The new complexes analyse satisfactorily for C, H, N, S, and Ni, and have also been characterised by mass and n.m.r. spectroscopy.

from (III) and (IV), which have 5 : 7 : 5-membered chelate ring systems, and with those obtained from (I) (5 : 5 : 5),


(I)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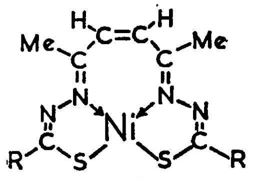
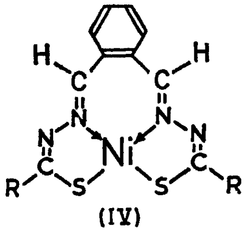

(III)


(IV)

Complex		$E_{\frac{1}{2}}{}^{a}$	$E_{\frac{1}{2}}{}^{a}$
(I; R^1 = NHMe; R^2 = R^3 = H)	..	−1·10	−1·80
(I; R^1 = NHMe; R^2 = H; R^3 = Me)	..	−1·22	−1·86
(I; R^1 = NH_2; R^2 = H, R^3 = Me)	..	−1·21	−1·82
(I; R^1 = NHMe; R^2 = R^3 = Me)	..	−1·37	−1·94
(I; R^1 = NH_2; R^2 = R^3 = Me)	..	−1·31	−1·89
(I; R^1 = NHMe; R^2,R^3 = $[CH_2]_4$)	..	−1·33[b]	−1·95
(II; R = NHMe)	..	−1·48	c
(III; R = NH_2)	..	−1·22	c
(III; R = NHMe)	..	−1·21[d]	c
(IV; R = NHMe)	..	−1·26	−1·79
(I; R^1 = Ph; R^2 = R^3 = Me) ..	..	−0·53[e]	−1·24[e]
$[Ni\{SC(Ph)NNH\}_2]^0$	..	−0·14[e]	−1·13[e]

[a] In volts; estimated error ±10 mv.; results *vs.* S.C.E.; [b] irreversible wave; [c] wave not observed, possibly because it was obscured by reduction of medium; [d] ill-defined wave; [e] recorded in Me_2SO (ref. 1).

shows that $E_{\frac{1}{2}}$ for the first wave in (II) is *ca.* 100 mv. more negative than that in (I; R^1 = NHMe, R^2 = R^3 = Me) whereas $E_{\frac{1}{2}}$ for the corresponding waves in (III) and (IV) is very similar to, or only 40 mv. more negative than, that in (I; R^1 = NHMe, R^2 = R^3 = Me). This would seem to imply that (IV), the best models of which indicate that the benzene ring is steeply tilted out of the NiN_2S_2 co-ordination plane, thereby destroying full conjugation, behaves as though it is planar and conjugated, like (I), but unlike (II). Because of the structural implications of these data, the relationship in chelate ring size between (II) and (IV), and the limited structural data on tetradentate complexes containing a seven-membered chelate ring, we have determined the crystal and molecular structures of (II) and (IV).

Compound (II) crystallises as pink prisms in the monoclinic space group $P2_1/c$; $Z = 4$, $a = 7{\cdot}54$, $b = 15{\cdot}02$, $c = 14{\cdot}68$ Å, $\beta = 112°\,14'$. Three-dimensional *X*-ray data have been collected by photographic methods, and comprise 2132 independent reflections; the current *R*-factor is 0·137. Compound (IV) crystallises as red plates in the orthorhombic space group, $P2_12_12_1$; $Z = 4$, $a = 17{\cdot}45$, $b = 17{\cdot}04$, $c = 4{\cdot}77$ Å. Three dimensional *X*-ray data (1111 independent reflections) have been collected by photographic methods and the structure has been refined to a current discrepancy index of 0·16. The structures of (II) and (IV) are shown in Figures 1 and 2, respectively.

In (II), the co-ordination around the nickel atom involves a distortion from square planarity such that the Ni-atom, the two S-atoms and one of the co-ordinated N-atoms are approximately coplanar (r.m.s. deviation 0·046 Å), whereas the remaining co-ordinated N-atom is 0·66 Å from this mean plane. Each of the thiosemicarbazide chelate fragments, SC(N)NN, is essentially planar, the planes being mutually inclined at an angle of 65°. The Ni-atom lies 0·7 Å 'below' each of the chelate planes, and the C-atoms adjacent to the co-ordinated N atoms lie 0·38 Å and 0·51 Å, respectively, 'above' the planes of the neighbouring chelate rings. Thus, it appears that constraint, imposed by the partially saturated seven-membered chelate ring system, causes the out-of-plane distortions of atoms which might otherwise be expected to form part of planar conjugated systems with the thiosemicarbazide fragments.

In (IV), the co-ordination around the Ni-atom is substantially planar; the two thiosemicarbazide chelate planes are mutually inclined at an angle of 33° and are symmetrically orientated with respect to the mean co-ordination plane of the nickel. The six-atom chelate plane is inclined at only 11° to the mean co-ordination plane of the Ni-atom, indicating that opportunities for electron delocalisation throughout the tetradentate ligand have greatly reduced out-of-plane distortions in the seven-membered chelate ring; strain is presumably relieved by in-plane, angular distortions.

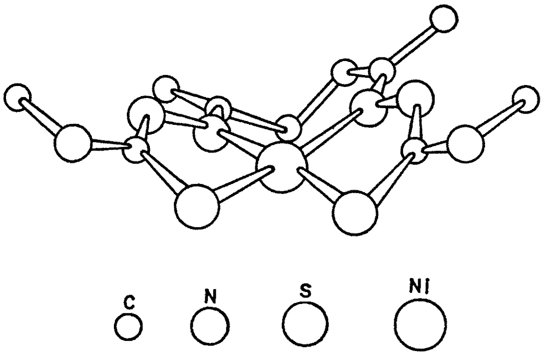


FIGURE 1

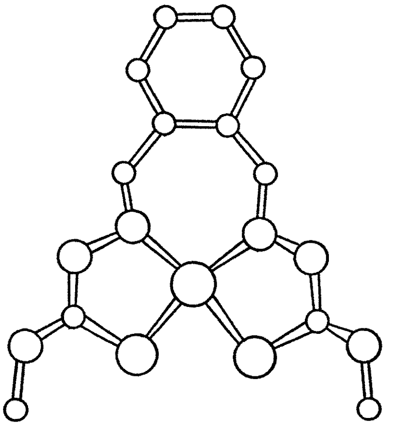


FIGURE 2

In both (II) and (IV), the geometries of the thiosemicarbazide fragments differ markedly from that found in bis(thiosemicarbazide)nickel(II)[4] where the two C–N bond lengths of 1·25 Å (in the chelate ring) and 1·44 Å (extra-ring), and the N–N length of 1·54 Å, indicate a substantially localised bonding system. The geometries resemble more closely those found in complexes of the protonated ligand, *i.e.* $Zn(NH_2NHCSNH_2)Cl_2$[5] and $Ni(NH_2NHCSNH_2)_2SO_4\cdot3H_2O$,[6] where a more extended delocalisation of π-electrons is suggested (N–C = 1·29; C–N = 1·31; N–N = 1·34 Å). Such delocalisation is facilitated in molecules (II) and (IV) by the inclusion of the thiosemicarbazide fragments in a partially or wholly conjugated tetradentate ligand.

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