# Chemical Communications

## High-spin Five-co-ordinate Nickel(II) Complexes with Salicylaldimine–Catechol Mixed Ligands

By L. SACCONI,* P. L. ORIOLI, and M. DI VAIRA

(*Istituto di Chimica Generale e Inorganica, Università di Firenze, Florence, Italy*)

HIGH-SPIN FIVE-CO-ORDINATE NICKEL(II) complexes have recently been described.[1] The first complex studied by $X$-ray analysis had the formula $(5\text{-Cl·Salen·NEt}_2)_2\text{Ni}^{II}$ (I) [2] and was formed from the Schiff base $5\text{-Cl·C}_6\text{H}_3(\text{OH})\text{·CH}:\text{N}[\text{CH}_2]_2\text{·NEt}_2$, derived from 5-chlorosalicylaldehyde and $NN$-diethylethylenediamine. In this complex, with its distorted square-pyramidal structure, one molecule of ligand acts as tridentate and the other one as bidentate. If one salicylaldimine molecule is substituted by a molecule of catechol, complexes with the general formula $(X\text{·Salen·NEt}_2)(\text{catec})\text{Ni}^{II}$ (II) are obtained. When $X = 5,6$-benzo, a red diamagnetic square-planar complex is formed. With $X = H$, 5-Cl, 5-Br, or 3,4-benzo, ochre-coloured paramagnetic complexes are formed with values of $\mu_{eff}$ varying from 3·24 to 3·33 B.M. Diffuse reflectance spectra of these compounds show crystal field bands at *ca.* 6700m, 9700w, 11,300sh, and 14,000m cm.$^{-1}$ (Figure 1). This type of spectrum compares well with the reflectance spectrum of the compound (I) which shows bands at 7700m, 9500w, 12,700w, and 16,500m cm.$^{-1}$. These bands were assigned as spin-allowed transitions from the $^3B_1$ ground-state to the excited states, all deriving from the $^3F$ state of the free ion, *i.e.* $^3E$, $^3A_2$, $^3B_2$, and $^3E$, respectively.[3] This spectrum, then, strongly suggests a five-co-ordinate structure for complexes of type (II).

A complete three-dimensional $X$-ray analysis on the unsubstituted derivative $(\text{Salen·NEt}_2)(\text{catec})\text{Ni}^{II}$ $(R = 11·6\%$ over 3800 observed reflections)

has shown that the structure consists of dimers of (II) formed by sharing one oxygen atom of each catechol molecule by the nickel(II) atoms. In
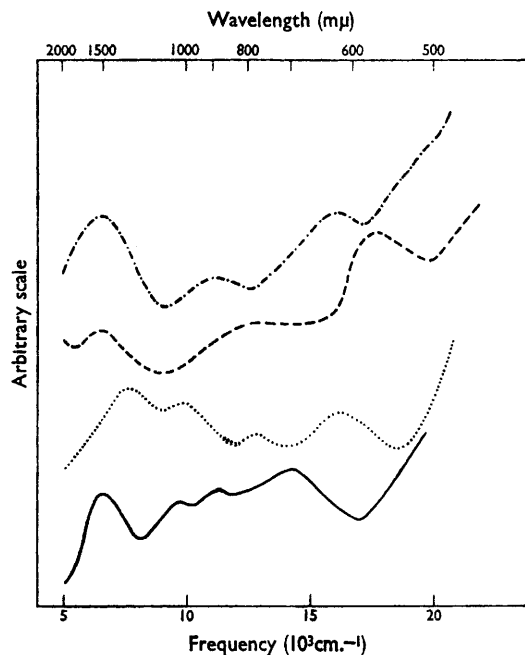


FIGURE 1. *Diffuse reflectance spectra of*: (Salen·NEt$_2$)-(catec)Ni$^{II}$ (———); (5-Cl·Salen·NEt$_2$)$_2$Ni$^{II}$ (· · ·); (Salen·NEt$_2$)(catec)Co$^{II}$ (- - -); (5-Cl·Salen·NEt$_2$)$_2$Co$^{II}$ (- · - · -).

these dimers the salicylaldimine acts as tridentate and the catechol monoanion as monodentate. In this way the nickel atom reaches the co-ordination number five. The other oxygen atom of the catechol molecule forms a strong hydrogen bond with the salicylaldimine oxygen atom (O · · · O distance = 2·50 Å). There are two crystallographically independent dimers in the cell, both possessing a centre of symmetry. Distances and angles in the two dimers show differences clearly beyond the errors, which will be discussed in a detailed paper. The values reported here refer respectively to the two dimers. The co-ordination polyhedron is intermediate between the trigonal bipyramid and the square pyramid. It can be described as a distorted trigonal bipyramid (Figure 2) with O(1), O(2'), and N(2) forming the equatorial plane and N(1) and O(2) in the axial
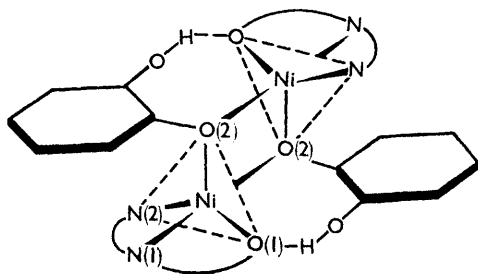
positions. The angles in the plane are: O(1)–Ni–O(2') = 117·0° (116·1°), O(2')–Ni–N(2) = 96·6° (100·7°), O(1)–Ni–N(2) = 146·2° (143·2°). The N(1)–Ni–O(2) angle is 177·8° (177·8°). Bond lengths about the nickel atom are: Ni–O(1) = 2·03 (1·96), Ni–O(2) = 2·03 (1·98), Ni–N(1) = 1·99 (1·96), Ni–N(2) = 2·15 (2·09), and Ni–O(2') = 1·94 (2·08) Å. The structure can alternatively be described in terms of a distorted square pyramid, with N(1), N(2), O(1), and O(2) forming the set of basal ligands and O(2') situated at the apex. The main distortion is caused by the atom N(2) which is depressed about 35° from the basal plane.

The dimeric structure disappears in solution, and the molecular weights of the various complexes in dichlorobenzene practically correspond to a monomeric formula. Absorption spectra in this solvent are similar to that of the diamagnetic 5,6-benzo-derivative, since they do not show any absorption below 13,000 cm.$^{-1}$.

The cobalt(II) complex, (Salen·NEt$_2$)(catec)-Co$^{II}$, is isomorphous with the nickel(II) derivative on the basis of their X-ray powder diagrams. Reflectance spectra of this compound and of other ring-substituted analogues agree well with the spectra of other five-co-ordinate cobalt(II) complexes with Schiff bases having known structure, e.g., (5-Cl·Salen·NEt$_2$)$_2$Co$^{II}$,[2,4] and bis-(N-methyl-salicylaldiminato)Co$^{II}$,[5] (Figure 1).

FIGURE 2. Distorted trigonal bipyramid structure of (Salen·NEt$_2$)(catec)Ni$^{II}$ (II).

[1] L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, Inorg. Chem., 1965, 4, 943; L. Sacconi, M. Ciampolini, and G. P. Speroni, J. Amer. Chem. Soc., 1965, 87, 3102; J. Lewis, R. S. Nyholm, and G. A. Rodley, Nature, 1965, 207, 72; L. Sacconi and I. Bertini, J. Amer. Chem. Soc., 1966, 88, 5180; P. L. Orioli, M. Di Vaira, and L. Sacconi, Chem. Comm., 1966, 300; M. Ciampolini and G. P. Speroni, Inorg. Chem., 1966, 5, 45; M. Ciampolini and N. Nardi, ibid., 1966, 5, 41.
[2] L. Sacconi, P. L. Orioli, and M. Di Vaira, J. Amer. Chem. Soc., 1965, 87, 2059; P. L. Orioli, M. Di Vaira, and L. Sacconi, ibid., 1966, 88, 4383.
[3] M. Ciampolini, Inorg. Chem., 1966, 5, 35.
[4] L. Sacconi, M. Ciampolini, and G. P. Speroni, Inorg. Chem., 1965, 4, 1116.
[5] P. L. Orioli, M. Di Viara, and L. Sacconi, Chem. Comm., 1965, 103; Inorg. Chem., 1966, 5, 400.