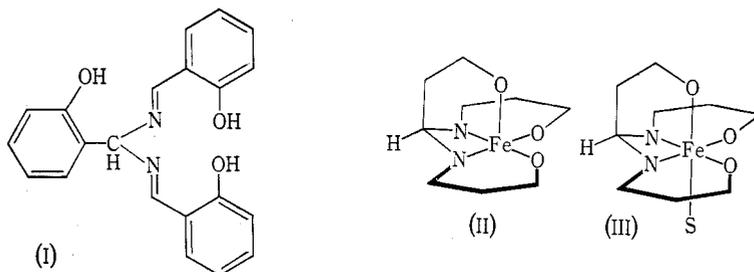


NICKEL(II) HYDROSALICYLAMIDE COMPLEXES*

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It is well known that salicylaldehyde condenses with ammonia to form the Schiff base hydrosalicylamide (I), which is a potential quinque-dentate ligand. The only metal complexes of this ligand which have so far been reported are neutral iron(III) complexes.¹ The simple iron(III) complex, $C_{21}H_{15}FeN_2O_3$, has been shown to be a five-coordinate non-electrolyte (II) which readily adds on solvent molecules to form six-coordinate adducts (III).



Previous attempts to prepare hydrosalicylamide complexes with divalent metals, such as copper(II) and nickel(II), by treating the ligand with metal acetate in methanol, have resulted in hydrolysis of the ligand and formation of salicylaldiminato complexes.²

By using a ligand exchange technique in a hydrocarbon solvent we have now succeeded in preparing a series of nickel(II) hydrosalicylamide complexes.

The starting point for these preparations was bis(*N*-octylsalicylaldiminato)-nickel(II). This compound (3 moles), dissolved in hot toluene, was added to a hot toluene solution of hydrosalicylamide (2 moles). On cooling, a pale green precipitate formed, which was filtered, dried, and washed with methanol to remove free organic material. Analysis of the *product* showed it to be $Ni_3L_2(H_2O)_2$, where L is the hydrosalicylamide anion, $C_{21}H_{15}N_2O_3^-$ (Found: C, 55.8; H, 3.8; N, 6.8; Ni, 19.8. $C_{42}H_{34}N_4Ni_3O_6$ requires C, 56.2; H, 3.8; N, 6.2, Ni, 19.7%).

The conditions of the preparation were quite critical. The presence of more than very small amounts of water or the use of incorrect proportions of reactants led to hydrolysis of the ligand and rapid precipitation of red crystals of bis(salicylaldiminato)nickel(II), which proved very difficult to separate from the hydrosalicylamide

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¹ Tsumaki, T., Antoku, S., and Shito, M., *Bull. chem. Soc. Japan*, 1960, **33**, 1096.

² Pfeiffer, P., Buchholz, E., and Bauer, O., *J. prakt. Chem.*, 1931, **129**, 163.

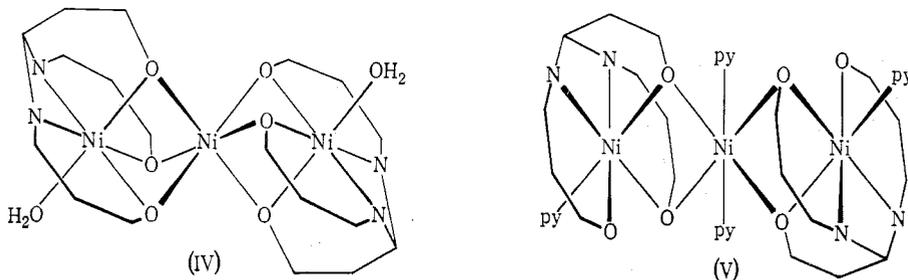
complex. The preparation was also achieved starting from other bis(*N*-alkylsalicylaldiminato)nickel(II) chelates.

By heating the dihydrate $\text{Ni}_3\text{L}_2(\text{H}_2\text{O})_2$ in dry nitrobenzene, nitromethane, chloroform, or heterocyclic bases, compounds were obtained of the type $\text{Ni}_3\text{L}_2\text{S}_x$, where S is the solvent. For most of these we were unable to obtain analyses corresponding to exact integral values of x , but the *pyridine compound* was quite readily obtained pure and had the formula $\text{Ni}_3\text{L}_2\text{py}_4$ (Found: C, 63.3; H, 4.6; N, 9.5; Ni, 14.7. $\text{C}_{62}\text{H}_{50}\text{N}_8\text{Ni}_3\text{O}_6$ requires C, 63.6; H, 4.3; N, 9.5, Ni, 14.9%).

This compound was soluble in toluene and the molecular weight obtained by vapour pressure osmometry at 37° was 1285 (calculated for $\text{Ni}_3\text{L}_2\text{py}_4$, 1179).

The hydrate $\text{Ni}_3\text{L}_2(\text{H}_2\text{O})_2$ and pyridine adduct $\text{Ni}_3\text{L}_2\text{py}_4$ were both green solids, with magnetic moments of 3.2 and 3.4 B.M. per nickel atom respectively. Visible-region reflectance spectra of both compounds showed absorption bands about 590 and 950 $\text{m}\mu$. In toluene solutions the pyridine adduct showed absorption bands at 605 $\text{m}\mu$ (ϵ 12) and 950 $\text{m}\mu$ (ϵ 12), and in pyridine solutions at 595 $\text{m}\mu$ (ϵ 15) and 950 $\text{m}\mu$ (ϵ 14). These data suggest that in both compounds all the nickel atoms have octahedral environments.

The infrared spectra of the two compounds in the 4–15 μ region are similar to that of hydrosalicylamide and quite different from both the original bis(*N*-octylsalicylaldiminato)nickel(II) and bis(salicylaldiminato)nickel(II). In the 1520–1560 cm^{-1} region there are significant differences between the spectra of $\text{Ni}_3\text{L}_2(\text{H}_2\text{O})_2$ and $\text{Ni}_3\text{L}_2\text{py}_4$. The former compound has only a single intense band at 1560 cm^{-1} , whereas the latter has twin bands at 1560 and 1540 cm^{-1} . On the basis of our previous observations on the infrared spectra of bridged Schiff base complexes of zinc,³ it seems likely that the single band at 1560 cm^{-1} in the hydrate indicates that in this compound all the phenolic oxygen atoms are bridging, whereas the double peak in the pyridine complex suggests that one of the two phenolic oxygen atoms adjacent to the azomethine group is non-bridging, although an alternative structure in which these two phenolic oxygen atoms are bridging might have been expected.



The magnetic properties and the visible-region and infrared data are thus consistent with the formulation of the two compounds as (IV) and (V).

When the *pyridine adduct* $\text{Ni}_3\text{L}_2\text{py}_4$ was heated on a thermogravimetric balance it lost weight equivalent to four molecules of pyridine at 140–160°. The

³ Batley, G. R., and Graddon, D. P., *Aust. J. Chem.*, 1967, **20**, 885.

residue on analysis approximated to Ni_3L_2 , but we were not able to obtain this compound in a pure state. A typical analysis for the compound, prepared in this way is: Found: C, 57.4; H, 3.5; N, 6.9. $\text{C}_{42}\text{H}_{30}\text{N}_4\text{Ni}_3\text{O}_6$ requires C, 58.4; H, 3.5; N, 6.6%. The compound was yellow-green and had a magnetic moment of 3.3 B.M. per nickel atom. It is probably polymeric.

These compounds are of some interest as the central chelate ring including two nitrogen atoms is four-membered. From models it is apparent that some distortion is necessary if all five donor atoms are to be coordinated. It is thus somewhat surprising that the phenolic groups all become ionized and coordinated rather than forming a compound of the type NiL with one un-ionized phenolic group per ligand.