

Guanidinium and Alkylammonium Ion Complexation by Nickel(II) Schiff Base Complexes

Ambrogio Giacomelli,^a Carlo Floriani,^{*b} and Giovanni Perego^c

^a *Istituto di Chimica Analitica and* ^b *Istituto di Chimica Generale dell'Università di Pisa, 56100 Pisa, Italy*

^c *Assoreni S.p.A., 20097 San Donato Milanese, Milano, Italy*

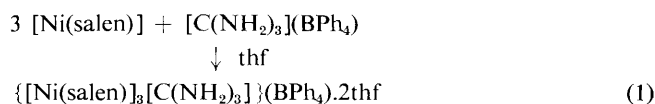
Guanidinium tetraphenylborate, $[\text{C}(\text{NH}_2)_3]\text{BPh}_4$, reacted with *N,N'*-ethylenebis(salicylideneaminato)nickel(II), $[\text{Ni}(\text{salen})]$, in thf to form $\{[\text{Ni}(\text{salen})]_3[\text{C}(\text{NH}_2)_3]\}(\text{BPh}_4) \cdot 2\text{thf}$, whose X-ray analysis showed that the guanidinium ion is encapsulated in a cage provided by the six oxygens of the three $[\text{Ni}(\text{salen})]$ units and held in place by six strong hydrogen bonds; the same complexation occurred using alkylammonium tetraphenylborate derivatives, which enhance significantly the solubility of nickel(II) Schiff base complexes in organic solvents.

The readiness with which some polynuclear complexes form from common 'complex ligands,' such as transition Schiff's base complexes, is well known.^{1,2} Thus, quadridentate Schiff's

base metal complexes can act as chelating agents of both transition and non-transition metal atoms, generating polynuclear systems.^{1,2} We were attracted by the use of such

'inorganic ligands' for complexing various cationic species,¹⁻³ the change of the reactivity of the transition metal as a consequence of such a complexation,⁴ the reactivity of the resulting polymetallic systems, and the use of cationic organic species as complex carriers in organic solvents.

Herein we report the 'complexation' of the guanidinium ion by *N,N'*-ethylenebis(salicylideneamino)nickel(II), [Ni(salen)], which yields what may be assumed to be an example of a novel class of organic substrates complexed by metal complexes without the intervention of the metal centre. [Ni(salen)], which is rather insoluble in tetrahydrofuran (thf) dissolved in the presence of guanidinium tetraphenylborate, [C(NH₂)₃]BPh₄, giving a deep-orange solution, from which, on standing, orange crystals of {[Ni(salen)]₃[C(NH₂)₃]}(BPh₄)·2thf were obtained,† equation (1). An X-ray crystallographic



study was required to prove the nature of the product.

Crystal data: triclinic, space group $P\bar{1}$; cell dimensions $a = 16.496(8)$, $b = 19.228(8)$, $c = 15.226(4)$ Å, $\alpha = 94.88(3)$, $\beta = 102.83(3)$, $\gamma = 123.81(3)^\circ$, $U = 3780.6$ Å³; $d_{\text{calc.}} = 1.316$ g cm⁻³ for $Z = 2$; Cu- K_α radiation ($\lambda = 1.54178$ Å); $\mu(\text{Cu-}K_\alpha) = 13.3$ cm⁻¹. 9249 independent reflections were collected in the range $2\theta \leq 110^\circ$ on an on-line Siemens AED diffractometer, using the $\theta - 2\theta$ scan method and 'five points' technique;⁵ 4687 reflections with $I > 4.5\sigma(I)$, where $\sigma^2(I) = [\text{total counts} + (0.005 I)^2]$, were used in the structure determination. The structure was solved by heavy-atom techniques; anisotropic refinement⁶ by block-diagonal least-squares converged to the unweighted $R = 0.058$.‡

The crystals are built up of discrete {[Ni(salen)]₃[C(NH₂)₃]}⁺ cations and BPh₄⁻ anions, and thf molecules of crystallization. In the complex cation, the guanidinium ion is surrounded by three [Ni(salen)] units; each NH₂ group interacts with two oxygens of two [Ni(salen)] so that six N-H...O hydrogen bonds are set up (see Figure 1). Additional interactions must probably be taken into account, because H(21) and H(22) really approach two oxygens, although with different geometry (see Figure 1). It appears questionable whether these interactions are to be regarded (or not) as weak hydrogen bonds.

The CN₃ moiety of the guanidinium ion is planar within 0.015 Å, but hydrogen bonding means that the hydrogen atoms are bent out of the CN₃ plane (the displacement ranging from 0.06 to 0.34 Å) towards the oxygen atoms of the salen units which also deviate (0.61–1.54 Å) from this plane. Rigorous planarity of the [C(NH₂)₃O₆] fragment is prevented by the surrounding salen ligands. The geometry of the [C(NH₂)₃] group compares well with that found for guanidinium salts.⁷ The range of C–N bond distances is wider, however, probably because of the non-uniform charge distribution on the guanidinium ion, a consequence of a non-symmetric hydrogen bonding framework. N(2) is more involved in the interaction with the salen units than N(1) and N(3); moreover, N(1) gives rise to N...O distances larger than do the other guanidinium nitrogen atoms (see Figure 1). Thus, the extent

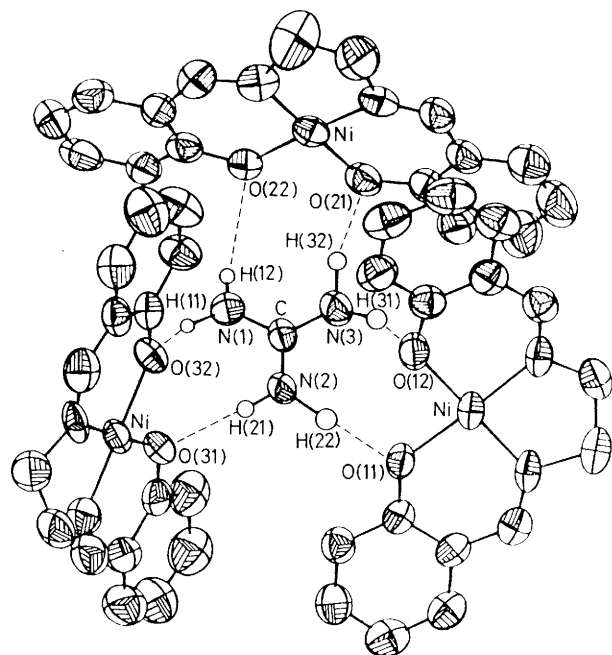


Figure 1. An ORTEP drawing of the macrocation {[Ni(salen)]₃[C(NH₂)₃]}⁺, excluding hydrogen atoms of salen. Bond distances (Å) and angles (°): C–N(1), 1.346(11); C–N(2), 1.299(12); C–N(3), 1.320(11); N(1)–C–N(2), 119.3(4); N(1)–C–N(3), 119.1(4); N(2)–C–N(3), 121.6(4). Hydrogen bond distances (Å) and angles (°) for [N–H...O] units:

	N...O	N–H	H...O	N–H...O
N(1)–H(11) O(32)	3.07	1.08(9)	2.10	148.1
N(1)–H(12) O(22)	3.11	0.75(7)	2.40	157.1
N(2)–H(21) O(31)	2.88	0.92(9)	2.01	157.6
N(2)–H(22) O(11)	2.92	1.14(8)	1.78	173.8
N(3)–H(31) O(12)	2.91	1.03(9)	1.99	148.4
N(3)–H(32) O(21)	2.83	1.02(9)	1.83	163.2
N(2)–H(21) O(32)	3.17	0.92(9)	2.57	123.8
N(2)–H(22) O(12)	3.12	1.14(8)	2.59	106.6

of hydrogen bonding associated with the individual nitrogen atoms decreases in the order N(2), N(3), N(1). Hydrogen bonding of a nitrogen atom results in a weakening of the N–H bond and a corresponding strengthening of the related C–N bond.⁸

The observed C–N bond distances agree with this, increasing from 1.299(12) Å, C–N(2), to 1.346(11) Å, C–N(1). The geometry of the [Ni(salen)]²⁺,⁹ and BPh₄¹⁰ units is in good agreement with that previously found in similar units. The atomic positions of thf, which is present as crystallization solvent, are poorly defined, as is often the case.¹¹

The special ability of guanidinium ion to act as a template agent in crown ether formation and to complex with the ethers once formed, has been widely explored by Cram *et al.*, who proposed a wreath-like host structure surrounding a guanidinium ion held in place by six hydrogen bonds.¹² [Ni(salen)] complexes alkylammonium tetraphenylborates, [RNH₃]BPh₄, as well as guanidinium tetraphenylborate. This result is rather attractive in view of the large number of organic molecules bearing –NH₃⁺ as a functional group. When provided with a suitable organic residue (*e.g.*, R = *n*-octyl), [RNH₃]BPh₄ produces highly concentrated thf solutions of [Ni(salen)]. When R = Buⁿ, an alkylammonium complex was isolated: {[Ni(salen)]₂(BuⁿNH₃)}BPh₄.† It is reasonable to assume that in all cases the anchoring of the organic molecule to the inorganic counterpart is determined mainly by the hydrogen bond formation.³ Complexation of guanidinium and alkyl-

† Satisfactory analytical data were obtained. The thf content depends on the crystallization and drying conditions.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

ammonium tetraphenylborate derivatives occurs with other tetradentate Schiff base complexes of transition metals.

The present results suggest that it will be possible to design and synthesize inorganic hosts for organic cations, which can act as template agents, bridging close more than one metal centre. This kind of complexation gives rise to a complex-anchored organic molecule, with the metal free for promoting the activation of other reactive sites of the same molecule.

Received, 11th March 1982; Com. 284

References

- 1 E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, 1969, **4**, 391; S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1805; C. J. O'Connor, D. P. Freyberg, and E. Sinn, *Inorg. Chem.*, 1979, **18**, 1077; K. A. Leslie, R. S. Drago, G. D. Stucky, D. J. Kitko, and J. A. Breese, *ibid.*, p. 1885; M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, 1972, 311.
 - 2 C. Floriani, F. Calderazzo, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 1973, 384; N. Bresciani-Pahor, M. Calligaris, P. Delise, G. Nardin, L. Randaccio, E. Zotti, G. Fachinetti, and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1976, 2310 and references cited therein; L. G. Armstrong, H. C. Lip, L. F. Lindoy, M. McPartlin, and P. A. Tasker, *ibid.*, 1977, 1771; H. Milburn, M. R. Truter, and B. L. Vickery, *ibid.*, 1974, 841; M. Pasquali, F. Marchetti, C. Floriani, and M. Cesari, *Inorg. Chem.*, 1980, **19**, 1198; G. Fachinetti, C. Floriani, P. F. Zanazzi, and A. R. Zanzari, *ibid.*, 1978, **17**, 3002; D. E. Fenton, N. Bresciani-Pahor, M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 1979, 39.
 - 3 E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 1970, 396, 400, and 406.
 - 4 S. Gambarotta, M. L. Fiallo, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1982, 503.
 - 5 W. Hoppe, *Acta Crystallogr., Sect. A*, 1969, **25**, 67.
 - 6 Isotropic thermal parameters were used for one of the two independent thf molecules and for the guanidinium hydrogen atoms. The contributions of the second thf molecule, which displays a disordered arrangement in the crystal, as well as the remaining hydrogen atoms, were kept fixed during the refinement. The calculations were performed by computer programs written by A. Immirzi, *Ric. Sci.*, 1967, **37**, 847; *J. Appl. Crystallogr.*, 1973, **6**, 246.
 - 7 J. M. Adams and R. W. H. Small, *Acta Crystallogr., Sect. B*, 1976, **32**, 832; *ibid.*, 1974, **30**, 2191.
 - 8 For a detailed discussion concerning the bonding mode of the methylguanidinium hydrogen atoms see: F. A. Cotton, V. W. Day, E. E. Hazen, and S. Larsen, *J. Am. Chem. Soc.*, 1973, **95**, 4834.
 - 9 M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, 1972, **7**, 385.
 - 10 M. Di Vaira and A. Bianchi-Orlandini, *J. Chem. Soc., Dalton Trans.*, 1972, 1704.
 - 11 L. Randaccio, *Gazz. Chim. Ital.*, 1974, **104**, 991.
 - 12 K. Madan and D. J. Cram, *J. Chem. Soc., Chem. Commun.* 1975, 427; E. P. Kyba, R. C. Helgeson, K. Madan, G. W. Gokel, T. L. Tarnowski, S. S. Moore, and D. J. Cram, *J. Am. Chem. Soc.*, 1977, **99**, 2564; D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, 1978, **11**, 8; J. M. Lehn, P. Vierling, and R. C. Hayward, *J. Chem. Soc., Chem. Commun.*, 1979, 296.
-