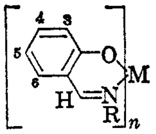
The Bromination of Salicylaldimine Chelates with N-Bromosuccinimide[1]

RUDOLPH W. KLUIBER

Department of Chemistry, Rutgers—The State University, Newark, New Jersey 07102

Received November 7, 1967

Bis(N-n-butylsalicylaldiminato)nickel(II) (I, M = Ni, R = C_4H_9, n = 2) has been reported to form a dibromide upon interaction with N-bromosuccinimide,[2] but some question exists as to whether the substitution occurs at the azomethine carbon[3] or at a ring phenyl position.[4] This substitution is now shown to occur on the ring, principally at the 5 position in agreement with the reactivity of salicylaldehyde[5] and with the observed reactivity of the chelated 2,4-pentanedionates.[2,6] Further interaction of the dibromide with N-bromosuccinimide also produces a tetrabromide which is bis(N-n-butyl-3,5-dibromosalicylaldiminato)nickel(II). These reactions have also been extended to the bromination of the kinetically inert complex tris(N-methylsalicylaldiminato)cobalt(III) (I, M = Co, R = CH_3, n = 3].



The structure of these chelates was demonstrated by analysis, independent synthesis, and by infrared, near infrared-visible, and nmr spectroscopy. The infrared data are in agreement with the indicated substitution with characteristic phenyl hydrogen out-of-plane deformation absorptions of proper intensity found at 750–760 cm^{-1} for the unsubstituted imine chelates, at 815–820 cm^{-1} for the 5-bromo chelates, and at 860 cm^{-1} for the 3,5-dibromo chelates.[7] In each case a strong absorption attributable to the imine C=N stretching frequency was observed at 1615–1630 cm^{-1}.[4] The spectra of chelates prepared by alternate methods were in each case identical. The visible-near infrared spectra of these chelates also were in each case similar to those previously reported for such cobalt(III)[8,9] and nickel(II)[10] complexes.

The nmr data support the assigned structures with the resonances due to the protons *ortho* and *para* to the oxygen having the proper intensity and, where definable, the proper splitting for the indicated substitution. The nickel chelate spectra were all concentration dependent in agreement with the known association of these materials in solution to produce mixtures of diamagnetic monomers having a square planar configuration around the nickel ion and paramagnetic polymeric species.[11,12] This phenomenon is particularly evident in the case of the 5-bromo chelate in which the azomethine proton resonance is shifted 0.58 ppm downfield. Such large shifts are attributable to spin delocalization in a paramagnetic complex and are in agreement with shifts previously observed for paramagnetic salicylaldimine complexes.[13-15] The effect of concentration on the spectra of the unsubstituted and 3,5-dibromonickel chelates is considerably less pronounced with the azomethine proton resonance being shifted downfield only 0.11 and 0.35 ppm over the same concentration range. The large effect found for the 5-bromo derivative is probably due to the electron-withdrawing effect of the bromo group which leaves the chelated nickel(II) ion more electrophilic. The smaller effect noted for the 3,5-dibromo derivative may be due to compensating effects of increased electrophilicity of the nickel ion and steric inhibition of association by the 3 substituent[11] and/or decreased nucleophilicity of the oxygen atoms due to electron withdrawal. Increasing the temperature of a 0.05 *M* deuteriochloroform solution of the 5-bromo derivative from 38 to 58° also shifts the position of the proton resonances, *e.g.*, the azomethine resonance is shifted from −670 to −702 cps, suggesting the additional presence of paramagnetic "tetrahedral" nickel(II) species in these solutions.[13,16] Some spectral evidence was found for both associated and "tetrahedral" species in concentrated benzene solutions of the 5-bromo chelate in the form of a very broad but weak absorption in the near-infrared region which could be resolved into at least two broad peaks with maxima centered approximately at 9500 and 7000 cm^{-1} [14,17] characteristic of "octahedral" and "tetrahedral" species.

Nmr studies on the brominated cobalt(III) complexes showed that in solution, both are diamagnetic indicating that no Co(II) species are present and both are present only in the sterically favorable *trans* stereochemistry around the octahedral cobalt(III) ion.[18] Both of these chelates crystalize as solvates which are only desolvated with difficulty.

Experimental Section

Bromides of Bis(N-*n*-butylsalicylaldiminato)nickel(II).—Bis(N-n-butyl-5-bromosalicylaldiminato)nickel(II) was prepared by mixing together an alcoholic solution of 10 g (0.05 mol) of 5-bromosalicylaldehyde and 12 g (0.16 mol) of n-butylamine and an aqueous solution of 6 g (0.025 mol) of nickel chloride hexahydrate. The product, after isolation by filtration and drying, was recrystallized from carbon tetrachloride–petroleum ether

---

[1] This work was supported by the Research Council of Rutgers, The State University, Newark, N. J.

[2] R. W. Kluiber, *J. Amer. Chem. Soc.*, **82**, 4839 (1960).

[3] F. P. Dwyer and D. P. Mellor, Ed., "Chelating Agents and Metal Chelates," Academic Press Inc., New York, N. Y., 1964, p 355.

[4] R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).

[5] K. Auwers and O. Burger, *Ber.*, **37**, 3929 (1904); E. Werner, *Bull. Soc. Chim. Fr.*, **46**, 277 (1886).

[6] J. P. Collman, *Angew. Chem., Intern. Ed. Engl.*, **4**, 132 (1965).

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964.

[8] A. Chakravorty, K. C. Kalia, and T. S. Kannan, *Inorg. Chem.*, **5**, 1623 (1966).

[9] H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jap.*, **37**, 1154 (1964).

[10] L. Sacconi, P. Paoletti, and G. DelRe, *J. Amer. Chem. Soc.*, **79**, 4062 (1957).

[11] R. H. Holm, *ibid.*, **83**, 4683 (1961).

[12] H. C. Clarke, K. Macvicar, and R. J. O'Brien, *Can. J. Chem.*, **40**, 822 (1962).

[13] A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, **4**, 26 (1965).

[14] R. H. Holm, and K. Swaminathan, *ibid.*, **2**, 181 (1963); **1**, 599 (1962).

[15] E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, *J. Amer. Chem. Soc.*, **84**, 3968 (1962).

[16] L. Sacconi, *J. Chem. Soc.*, 4608 (1963).

[17] L. Sacconi, M. Ciampolini, and N. Nardi, *J. Amer. Chem. Soc.*, **86**, 819 (1964).

[18] A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1521 (1964).

(30–60°). The green needles thus obtained,[19] mp 193–195° [λ_{max}, 620 mμ (ϵ 95 cm^{-1} M^{-1}), benzene, 25°, nmr resonances ($CDCl_3$, 38°, 0.025 M), -N=CH (−626), -NCH_2, (−257), *o*-CH (−376), *m*,*m*-CH, (−433), CH_3CH_2 (−100), -CH_3 (−58 cps)] were identical in all respects with the dibromide[2] prepared by the N-bromosuccinimide bromination of bis(N-*n*-butylsalicyaldiminato)nickel(II). This starting chelate had the following resonances ($CDCl_3$, 38°, 0.02 M): -N=CH (−579), NCH_2 (−241), *o*-CH (−386), *p*-CH (−380), *m*,*m*-CH (−422, −430), CH_2CH_2 (−100), CH_3, (−58 cps).

Bis(N-*n*-butyl-3,5-dibromosalicylaldiminato)nickel(II) was prepared by the reaction of 4.1 g (0.01 mol) of bis(N-*n*-butylsalicylaldiminato)nickel(II) in 30 ml of chloroform with 7.1 g (0.04 mol) of powdered N-bromosuccinimide. After 1 hr the product was isolated by precipitation with petroleum ether, removal of the succinimide by vacuum sublimation at 110°, and recrystallization of the crude product from carbon tetrachloride. The green tetrabromide, mp 214–216° [λ_{max}, 620 mμ (ϵ 107 cm^{-1} M^{-1}), benzene, 25°; nmr resonances (38°, $CDCl_3$, 0.025 M), -NCH, (−556), -NCH_2 (−246), *m*,*m*-CH, (−430, −454), CH_2CH_2 (100), -CH_3 (−60 cps)] was identical with a chelate prepared as in the above paragraph using 7 g of 3,5-dibromosalicylaldehyde, 8 g of *n*-butylamine, and 3 g of nickel chloride hexahydrate.

Anal. Calcd for $C_{22}H_{24}Br_4N_2NiO_2$: C, 36.36; H, 3.33; N, 3.86; Ni, 8.08. Found: C, 36.54; H, 3.43; N, 3.72; Ni, 7.63.

Bromination of Tris(N-methylsalicylaldiminato)cobalt(III).—To 1.54 g (0.0032 mol) of tris(N-methylsalicylaldiminato)cobalt(III),[18] recrystallized from xylene [λ_{max}, 387, 572 sh, 637 mμ sh, (ϵ 8900, 275, —cm^{-1} M^{-1}), benzene, 25°] in 15 ml of chloroform was added 1.8 g (0.01 mol) of powdered N-bromosuccinimide. After 2 hr of stirring, the chloroform was removed by distillation and the succinimide was removed by sublimation at 110° under vacuum to yield 2.34 g (100%) of crude tribromo chelate. This was purified by recrystallization from approximately 30 ml of xylene to yield 1.20 g (54% yield) of tris(N-methyl-5-bromosalicylaldiminato)cobalt(III), mp 279–281°, identical with an authentic sample,[20] mp 283–285° [λ_{max}, 396, 575 sh, 648 sh mμ (ϵ 8900, 355, —cm^{-1}M^{-1}), benzene, 25°]. The brominated chelate forms a 1:1 solvate with xylene, as evidenced by elemental, infrared, and nmr analysis, which was only slowly desolvated at 140° under vacuum.

Anal. Calcd for $C_{32}H_{31}Br_3CoN_3O_3$: C, 47.79; H, 3.88; N, 5.22; Co, 7.33. Found: C, 48.26; H, 4.18; N, 5.25; Co, 7.36.

A hexabromide was prepared by the above procedure using 1.54 g of unbrominated cobalt(III) complex and 3.6 g of N-bromosuccinimide. Isolation of the very insoluble product as above yielded 2.96 g of crude material and 2.24 g (71%) of pure tris(N-methyl-3,5-dibromosalicylaldiminato)cobalt(III) recrystallized from xylene and dried at 140° under vacuum. Under these conditions the solvent was removed only with great difficulty. The chelate also was found to be rather insoluble in most common solvents except at high temperatures, and the nmr spectrum of this chelate was obtained in a nitrobenzene solution. An authentic sample of this material was prepared from 3,5-dibromosalicylaldehyde by the method of West[21] and melted at 302–303° dec [λ_{max}, 395, 590, 654 sh mμ (ϵ 9400, 430, . . . cm^{-1} benzene, 25°].

Anal. Calcd for $C_{24}H_{18}Br_6CoN_3O_3$: C, 30.84; H, 1.94; N, 4.50; Co, 6.30. Found: C, 31.39; H, 2.16; N, 4.60; M^{-1}) Co, 5.80.

Spectra.—The infrared spectra were obtained using the Nujol mull technique, sodium chloride plates, and a Beckman Model 10 grating instrument. The near-infrared spectra and the visible spectra were obtained using a Cary Model 14 spectrometer using benzene solutions or Nujol mulls mounted on filter paper. Nmr spectra were obtained using deuteriochloroform solutions with tetramethylsilane as an internal standard. All spectra were recorded using a Varian 60 Mc/sec fixed-frequency instrument with the downfield direction being considered as the negative direction. Melting points were recorded using a Mel-Temp apparatus.

---

[19] V. V. Zelentsov, I. A. Savich, and V. B. Eudokimov, *Nauchn. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol*, 672 (1958); *Chem. Abstr.*, **53**, 5789 (1959).

[20] J. Endo, *Nippon Kagaku Zasshi*, **65**, 428, 667 (1944); *Chem. Abstr.*, **42**, 1576 (1948).

[21] B. O. West, *J. Chem. Soc.*, 4944 (1960).