

Tetraphenylborate Salts of some Tridentate Chelates of Nickel(II)

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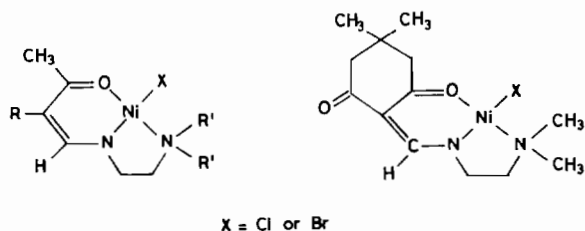
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Abstract

Tetraphenylborate salts of nickel(II) complexes have been prepared where the nickel(II) is bound to the tridentate Schiff base adducts of unsymm.-*N,N*-dimethyl or -*N,N*-diethylethylenediamine and the β -dicarbonyl compound, $\text{CH}_3\text{COCHRC(O)H}$, $\text{R} = \text{CH}_3\text{CO}$ or $\text{C}_2\text{H}_5\text{OCO}$ or 2-acetyl-5,5-dimethyl-1,3-cyclohexanedione. The synthesis involves reacting the chloro or bromo derivatives of the tridentate nickel(II) complexes with sodium tetraphenylborate in dichloromethane. Replacing the halo ligand by the noncoordinating tetraphenylborate ion results in some unusual coordinate bonding. For the $\text{CH}_3\text{-COCHRC(O)H}$ tridentate ligands, a dinuclear +1 cation is formed with two tridentate-nickel(II) groups bound to one another by a bridging hydroxyl ligand. For 2-acetyl-5,5-dimethyl-1,3-cyclohexanedione in the solid state, the free carbonyl of a tridentate ligand bound to a nickel(II) ion occupies the fourth coordinate site of a second nickel(II) ion. In acetone solution, the fourth coordinate position is believed to be occupied by the solvent.

Introduction

Chloro and bromo nickel complexes have been reported for the tridentate Schiff base adducts of unsymm.-*N,N*-dimethyl and -*N,N*-diethylethylenediamine and the β -dicarbonyl compound, $\text{CH}_3\text{-COCHRC(O)H}$ (1, 2) or $\text{C}_2\text{H}_5\text{OCO}$ (3) or 2-acetyl-5,5-dimethyl-1,3-cyclohexanedione (4) [1].



- 1 ($\text{R} = \text{CH}_3\text{CO}$, $\text{R}' = \text{CH}_3$)
 2 ($\text{R} = \text{CH}_3\text{CO}$, $\text{R}' = \text{C}_2\text{H}_5$)
 3 ($\text{R} = \text{C}_2\text{H}_5\text{OCO}$, $\text{R}' = \text{CH}_3$)

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The complexes are stable, diamagnetic materials in both the solid state and in solution. The resistance of these complexes to decomposition by moisture is greater than that of alkyl Schiff base complexes, presumably due to the presence of the halo ligand [2]. We have prepared other derivatives such as azide, nitrite and para-nitrophenylate by replacing the bromo or chloro ligands. If a bidentate ligand is substituted for a halo ligand, 5-coordinate nickel complexes result.

The question pursued here is what would happen when the halogen is replaced by a non-coordinating group, 3-coordinated nickel(II) being unstable [3]. Tetraphenylborate was selected because it is known as a non-associating counter-ion due to its symmetry and to the bulky phenyl groups [4]. The source of the tetraphenylborate will be the sodium salt since the sodium cation will help drive the exchange reaction to completion by the precipitation of the sodium halide salt. Complexes of cyanotriphenylborate are also prepared in an effort to distinguish between the reactivity toward halo-tridentate nickel(II) complexes of the non-coordinating $\text{B}(\text{C}_6\text{H}_5)_4^-$ ion and the coordinating $\text{NCB}(\text{C}_6\text{H}_5)_3^-$ ion.

Experimental

A solution of the halo-tridentate nickel(II) complex was added to an equimolar amount of the sodium tetraphenylborate or sodium cyanotriphenylborate in dichloromethane. After the mixture was stirred overnight, the reddish or orange solution was filtered to remove the sodium chloride. When the solvent was removed, a reddish or orange solid remained which was then recrystallized or reprecipitated.

Compounds

- 1, when $\text{X} = \text{NCB}(\text{C}_6\text{H}_5)_3$
 Cyanotriphenylborato [3-[[[2-(dimethylamino)-ethyl]imino]methyl]-2,4-pentanedionato- $\text{N}^3, \text{N}^3, \text{O}^2$]-

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nickel(II). Orange, melting point (m.p.) 230–232 °C. *Anal.* Calc. for $C_{29}H_{32}N_3O_2BNi$: C, 66.21; H, 6.51; N, 8.00; B, 2.06. Found: C, 66.22; H, 6.31; N, 7.92; B, 2.20%.

2, when $X = NCB(C_6H_5)_3$

Cyanotriphenylborato[3-[[[2-(diethylamino)ethyl]imino]methyl]-2,4-pentanedionato- N^3, N^3, O^2]-nickel(II). Orange, m.p. 185–187 °C. *Anal.* Calc. for $C_{31}H_{36}N_3O_2BNi$: C, 67.43; H, 6.57; N, 7.61; B, 1.96. Found: C, 66.24; H, 6.62; N, 7.41; B, 2.04%.

1, when $X = B(C_6H_5)_4$

Tetraphenylborato, hydroxy bis[3-[[[2-(dimethylamino)ethyl]imino]methyl]-2,4-pentanedionato- N^3, N^3, O^2]-nickel(II). Red, m.p. 153–154 °C. *Anal.* Calc. for $C_{44}H_{55}N_4O_5BNi_2$: C, 62.31; H, 6.54; N, 6.63; B, 1.28. Found: C, 61.69; H, 6.43; N, 6.53; B, 1.54%.

3, when $X = B(C_6H_5)_4$

Tetraphenylborato, hydroxy bis(ethyl-2[[[2-(dimethylamino)ethyl]imino]methyl]-3-oxobutanoato- N^2, N^2, O^3]-nickel(II). Red, m.p. 163.8–164.0 °C. *Anal.* Calc. for $C_{46}H_{59}N_4O_7BNi_2$: C, 60.83; H, 6.55; N, 6.19; B, 1.19. Found: C, 60.90; H, 6.46; N, 6.09; B, 1.28%.

4, when $X = B(C_6H_5)_4$

Tetraphenylborato[2-[N -[2-(dimethylaminoethyl)acetimidoyl]-5,5-dimethyl]1,3-cyclohexanedionato]-nickel(II). Orange, m.p. 173–175 °C. *Anal.* Calc. for $C_{38}H_{43}N_2O_2BNi$: C, 72.53; H, 6.89; N, 4.45; B, 1.72. Found: C, 66.19; H, 6.70; N, 4.30; B, 1.68%.

The percent carbon in boron containing compounds is often found to be low due to the formation of boron carbides [5].

A solution of 3 ($X = B(C_6H_5)_4$) in methanol was mixed with an equimolar solution of potassium chloride in methanol, and a white precipitate appeared. After being stirred for several hours, the solution was filtered. The solid was washed with methanol and dried (yield 90% of theory). The infrared spectrum of the solid in KBr was identical to that of potassium tetraphenylborate. The solvent was evaporated from the filtrate to yield a red oil. Workup of the oil indicated that it was in part the halo tridentate nickel complex, and in part, decomposition products.

The Fast Atom Bombardment, FAB, mass spectra were taken using sulfolane as the matrix. We wish to thank Phil Briggs of the Department of Chemistry, Harvard University for these spectra. The NMR spectra were taken on a Varian EM 390 spectrometer. Deutero-chloroform and deutero-acetone were used as the solvents. The Evans method was used to measure the solution magnetic susceptibilities [6]. The conductivity measurements were taken on a YSI

Model 31 conductivity bridge using acetone as the solvent. Magnetic susceptibilities of the solids were obtained by means of a Faraday Balance. Diamagnetic contributions were calculated using Pascal's constants [7]. UV spectra were taken on a Model 552 Perkin-Elmer spectrometer using acetone as the solvent. IR spectra were taken on a Model 1310 Perkin-Elmer spectrometer with the samples suspended in KBr, Nujol or Fluorolub.

Results and Discussion

When the halogen in the halo tridentate nickel complexes was replaced by cyanotriphenylborate, orange solids were produced. Proton resonance data and combustion analysis indicated the products were the anticipated one-to-one complexes of the nickel tridentate cation and the cyanotriphenylborate anion. The electronic spectra (Table I) and the magnetic susceptibilities support a diamagnetic, square-planar structure. The low electrical conductivity and the short wavelength maxima (Table I) suggest the coordination is strong even in acetone solution. Presumably the cyanotriphenylborato ligand is bound to the nickel through the nitrogen of the cyano substituent. The infrared spectra also indicate this type of a coordination by showing an increase in the C–N stretching frequency as a result of the bonding of the ligand to nickel, a shift reported for other cyano complexes [8]. For example, in sodium cyanotriphenylborate the band occurs at 2160 cm^{-1} for a KBr medium, whereas a band is seen at 2200 cm^{-1} in the spectrum of the cyanotriphenylborato complex of the tridentate chelate (1).

Reaction of sodium tetraphenylborate with the chloro derivative of the tridentate complex, (4), produced a one-to-one salt. The solid was diamagnetic, but not crystalline. In acetone solution, the

TABLE I. Electrical Conductivity and Visible Electronic Spectra of 10^{-3} M Acetone Solutions

Compound	Conductivity (mho cm^{-1})	λ_{max} (nm)	ϵ ($\text{M}^{-1}\text{ cm}^{-1}$)
$(C_2H_5)_4NCl$	110		
$NaNCB(C_6H_5)_3$	93		
$NaB(C_6H_5)_4$	120		
1 X = Cl	2	510	250
X = $NCB(C_6H_5)_3$	9	460	275
X = $B(C_6H_5)_4$	90	474	310
2 X = Cl	1	514	250
X = $NCB(C_6H_5)_3$	10	474	250
X = $B(C_6H_5)_4$	85	480	370
3 X = Cl	5	517	240
X = $NCB(C_6H_5)_3$	9	460	240
X = $B(C_6H_5)_4$	95	495	175

material was slightly paramagnetic as indicated by both the Evans method (1.1 BM) and the chemical shifts of the ligand protons. The chloro and cyanotriphenylborate derivatives of **4** exhibit a strong absorbance at 1625 cm^{-1} in the infrared spectra using a KBr medium. On the other hand, the tetraphenylborato analog shows no such band. Presumably the band is shifted to lower frequency and is hidden under the intense 1530 cm^{-1} absorbance exhibited by all three derivatives. The 1625 cm^{-1} band has been assigned to the stretching frequency of the free carbonyl group of the tridentate ligand in the nickel complex. It appears that this carbonyl group becomes coordinated to nickel in the tetraphenylborato analog and thus occupies the fourth coordination site about the nickel ion.

The peak integration in the PMR spectra of complexes **1** and **3** with $X = \text{B}(\text{C}_6\text{H}_5)_4$ suggests that the ratio of tridentate ligand to phenyl groups is 2:4 rather than the 1:4 ratio anticipated for a one-to-one complex of a tridentate nickel cation and a tetraphenylborate anion. The combustion analysis of the two compounds supports the 2:4 ratio. The tetraphenylborate ion can react with the loss of two phenyl groups [4]. Such a reaction would be consistent with the 2:4 or 1:2 ratio of tridentate ligand to phenyl group. The following evidence, however, strongly supports the presence of the tetraphenylborate group in the two complexes. First, by treating a methanol solution of complex **3** ($X = \text{B}(\text{C}_6\text{H}_5)_4$) with potassium chloride, a precipitate formed which was identified as potassium tetraphenylborate by its infrared spectrum. The yield of the reaction was greater than 95%. Second, both the infrared and negative ion FAB MS spectra of the complexes **1** and **3** ($X = \text{B}(\text{C}_6\text{H}_5)_4$) indicate the presence of the tetraphenylborate group. Third, by positive ion FAB MS, ions corresponding to Ni(tridentate ligand) and Ni_2 (tridentate ligand)₂ were observed. The PMR spectra also show that the tridentate ligand has remained intact in the complex. Since + and - FAB is a soft ionization method, little fragmentation is produced, and any decomposition products would be more readily observed than with conventional EI mass spectroscopy. Thus, it appears that both the ligand and the tetraphenylborate anion have not been altered in the synthesis of the tetraphenylborato derivatives of the tridentate nickel chelates. Fourth, quantitative analysis of the nickel in complex **3** ($X = \text{B}(\text{C}_6\text{H}_5)_4$) using dimethylglyoxime indicates a 13.0 weight percent nickel which is appropriate for Ni_2 (tridentate ligand)₂ $\text{B}(\text{C}_6\text{H}_5)_4$. Note that the species, Ni(tridentate)B(C₆H₅)₄ has only a 7.1 weight percent nickel.

Electrical neutrality requires the presence of another anion in the Ni_2 (tridentate)₂ $\text{B}(\text{C}_6\text{H}_5)_4$ species since each nickel has a charge of +2 and each ligand and tetraphenylborate have a charge of -1.

The infrared spectrum of **3** ($X = \text{B}(\text{C}_6\text{H}_5)_4$) for both KBr and Fluorolub media contains a sharp band at 3540 cm^{-1} which indicates the presence of an OH group. Since the material is analytically pure and has been dried *in vacuo* at $100\text{ }^\circ\text{C}$, any water present must be strongly associated with the complex. The evidence suggests that a bridging hydroxyl ligand binding the two nickel ion accounts for the neutral charge and the square planar geometry of the compound (red and diamagnetic). Each nickel(II) ion is coordinated to a tridentate ligand and the OH bridge. The hydroxyl bridge was most likely produced from adventitious moisture present in either the sodium tetraphenylborate or in the atmosphere during the synthesis. Furthermore, Osborn and his coworkers reported that a dinuclear copper complex acquired a bridging hydroxyl group when it was dissolved in water [9a]. A space filling model of the bridged dimer suggests that the *trans*-conformation has considerably less steric interference than the possible *cis* form.

In a number of hydroxyl bridged Cu(II) compounds, the IR stretch of the hydroxyl group appears in the range of 3400 to 3500 cm^{-1} [9, 10]. Mandal and Nag reported 3540 cm^{-1} for the OH stretch in some bis Cu(II) complexes [10c]. The value of the stretching frequency does not distinguish between a terminal and bridging OH group. For some manganese(II) complexes, the bridging OH group absorbs at 3530 cm^{-1} [11, 12]. The number of coordination compounds containing one hydroxyl bridge is small. Hodgson in his review of bridging dimeric compounds of the first row transition metals listed only one type of single bridge, that of the rhodo and erythro binuclear chromium(III) amine complexes [13, 14]. Since the review article appeared, single bridging hydroxyl compounds have been reported for several copper complexes [9], however, to date we have not found examples of bridging hydroxyl ligands in nickel(II) complexes. In the case of hydroxyethyl- and hydroxypropyl-salicylaldehydes, dimers and trimers are formed with nickel [15, 16]. These dimers are octahedral with paramagnetic nickel(II), and the bridging atoms are usually the phenolic oxygens [17].

The dimeric structure of the tetraphenylborato adduct of the complex with the tridentate ligand (**1**) remains a mystery because no OH stretching frequency is observed in its infrared spectrum.

The absence of coordination between the tetraphenylborate ion and nickel(II) is supported by the electrical conductivity data for acetone solutions (Table I) which show a significantly higher conductance for $X = \text{B}(\text{C}_6\text{H}_5)_4$ than for the $X = \text{Cl}$ or $X = \text{NCB}(\text{C}_6\text{H}_5)_3$ analogs. The visible absorbance maxima place the B(C₆H₅)₄ ligand between the other two in a spectrochemical series, but this does not conflict with the conductivity data if it is assumed that in

acetone solution, the solvent and not the $B(C_6H_5)_4$ group is bonded to the nickel(II) ion.

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References

- 1 G. Dudek and E. P. Dudek, *Inorg. Chim. Acta*, **8**, 219 (1974).
- 2 (a) G. W. Everett, Jr. and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2117 (1965); (b) Y. Y. Chin, E. E. Chu, B. D. McKinney, L. J. Willis and S. C. Cummings, *Inorg. Chem.*, **20**, 1885 (1981).
- 3 E. G. Jaeger, *Z. Chem.*, **6**, 111 (1966).
- 4 (a) Gmelin Borverbindungen Teil 8, Band 33, (1976); (b) R. B. King and K. C. Nainan, *J. Organomet. Chem.*, **65**, 71 (1974); (c) D. W. Slocum, B. Conway, M. Hodgman, K. Kuchel, M. Moronski, R. Noble, K. Webber, S. Duraj, A. Siegel and D. A. Owen, *J. Macromol. Sci., Chem.*, **A16**, 357 (1981).
- 5 G. Schmid and H. Noth, *Chem. Ber.*, **100**, 2899 (1967).
- 6 D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
- 7 P. W. Selwood, 'Magnetochemistry', Interscience, New York, 1943, p. 51.
- 8 (a) K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York, 1963, p. 167; (b) S. J. Lippard and Welcker, *Inorg. Chem.*, **11**, 6 (1972).
- 9 (a) P. L. Burk, J. A. Osborn and M. T. Youinou, *J. Am. Chem. Soc.*, **103**, 1273 (1981); (b) G. D. Fallon, K. S. Murray, B. Spethmann, J. K. Yandell, J. H. Hodgkin and B. C. Loft, *J. Chem. Soc., Chem. Commun.*, 1561 (1984); (c) J. R. Ferraro and W. R. Walker, *Inorg. Chem.*, **4**, 1382 (1965).
- 10 (a) W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **27**, 1063 (1965); (b) P. K. Coughlin and S. J. Lippard, *J. Am. Chem. Soc.*, **103**, 3228 (1981); (c) S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 2141 (1984).
- 11 W. M. Coleman and L. T. Taylor, *Inorg. Chem.*, **16**, 1114 (1977).
- 12 V. Baran, *Coord. Chem. Rev.*, **6**, 65 (1971).
- 13 D. J. Hodgson, in S. J. Lippard (ed.), *Prog. Inorg. Chem.*, **19**, 173 (1975).
- 14 M. S. Haddad, S. R. Wilson, D. J. Hodgson and D. N. Hendrickson, *J. Am. Chem. Soc.*, **103**, 384 (1981).
- 15 H. A. O. Hill and N. Zarb-Adami, *J. Inorg. Nucl. Chem.*, **37**, 2443 (1975).
- 16 J. A. Bertrand and C. E. Kirkwood, *Inorg. Chim. Acta*, **4**, 192 (1970).
- 17 R. J. Butcher, C. J. O'Connor and E. Sinn, *Inorg. Chem.*, **20**, 3486 (1981).