(c) **Preparation of the Tetracyanoethylene Complex. RhCl-(PPh$_3$)$_2$(t-BuNC)(TCNE)·CH$_2$Cl$_2$.**—The parent complex (2a, 40 mg) was mixed with an excess of TCNE in benzene, and the suspension was heated at 60–65° for 1 hr with stirring to give a yellow precipitate (30 mg) which was recrystallized from warm dichloromethane. The lemon yellow crystals were stable in air, ir (CH$_2$Cl$_2$) 2227 (for $\nu_{C\equiv N}$ of coordinated TCNE) and 2196 cm^{-1} (for $\nu_{C\equiv N}$ of t-BuNC).

(d) **Bromosulfatobis(triphenylphosphine)(*tert*-butyl isocyanide)(sulfur dioxide)rhodium, RhBr(SO$_4$)(PPh$_3$)$_2$(t-BuNC)(SO$_2$) (5).**—When added to liquid sulfur dioxide, 1d readily reacted with it to give a yellow solution which on evaporation gave a yellow powder: ir (Nujol) 2200 ($\nu_{C\equiv N}$), 1265, 1150, 1030, 870, and 660 cm^{-1} (for coordinated SO$_2{}^{21}$ and SO$_4{}^{2-}$).

Stabilization of High Oxidation States of Nickel with Pyridine Oxime Ligands

BY RUSSELL S. DRAGO* AND EVERETT I. BAUCOM[1]

In this article we report the preparation, isolation, and characterization of nickel(III) complexes with *syn*-2-benzoylpyridine oxime and *syn*-2-phenacylpyridine oxime. Various criteria are employed to establish the oxidation state of nickel. These findings are employed to extend and support a model reported earlier to account for the stability of a nickel(IV) complex of 2,6-diacetylpyridine dioxime.

Introduction

An earlier report from this laboratory[2] described the preparation and characterization of a nickel(IV) complex and suggested a model which described the ligand properties that stabilize the high oxidation state. Clearly, any models that attempt to explain how unusual oxidation states can be stabilized must be based on a semiempirical approach and consequently require the right input information. Incorrect input has given rise to many incorrect notions in this area.[3-9] In this article, we extend our earlier study on oxime ligands and provide evidence for the existence of a nickel(III) complex.

The literature is filled with reports of complexes which are claimed to be Ni(III), but subsequent work showed the claim to be incorrect. The potential difficulties in determining the oxidation state are exemplified in the work by Foust and Soderberg,[3] who showed that the complexes originally formulated as bromo- and iodobis(diphenylglyoximato)nickel(III) were in fact inclusion-like compounds of nickel(II) with halogen atoms sandwiched between layers of the planar bis(diphenylglyoximato)nickel(II). The observed epr spectra gave g values near 2.01. The halogen atoms apparently interacted with the phenyl rings of the complex rather than the metal, forming molecular inclusion complexes.

During the early to mid 1960's, a large number of dithiolate complexes, formulated as square-planar nickel(III), were reported.[4] Numerous later studies showed these complexes to be in fact cation-stabilized radical ligand compounds. In particular, Davidson, *et al.*,[5] showed that the ^{61}Ni hyperfine splitting in one of the "nickel(III)" dithiolate complexes amounted to only 4.5 G, indicating that little unpaired spin resided on the nickel atom. Numerous "nickel(III)" complexes similar to the dithiolates were shown to fit into the same overall pattern, as cation-stabilized radicals,[6] *e.g.*, paramagnetic[7] [Ni(diars)$_2$Cl$_2$]Cl (diars = *o*-phenylenebis(dimethylarsine)), a series of complexes[8] [Ni-(diars)$_2$X$_2$]Y (X$^-$ = Br$^-$, SCN$^-$, I$^-$; Y$^-$ = Br$^-$, SCN$^-$, I$^-$, ClO$_4{}^-$, $^1/_2$PtCl$_6{}^{2-}$) (μ ranged from 1.88 to 1.96 BM), and a triarsinenickel(III) complex[9] NiTBr$_3$ {T = CH$_3$As[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]}. A recent study[10] showed the complex Ni(diars)$_2$Cl$_2{}^+$ to be best described as a nickel(II)-stabilized diarsine radical. The primary arguments supporting this description of the complex, as opposed to the nickel(III) designation, were g values (powder and frozen ethanol solutions) of 2.05, 2.09, and 2.14 with arsenic hyperfine splitting of 23 G. Furthermore, preliminary crystal data showed that the nickel–arsenic bond distance increased on oxidation of the parent nickel(II) complex.

Some of the more believable claims for nickel(III) complexes will be summarized. Klemm, Brandt, and Hoppe[11] reported the preparation of the violet complexes K$_n$(Na)$_{3-n}$NiF$_6$ by the fluorination of K(Na)Cl–NiSO$_4$ mixtures.

Curtis and Cook[12] claimed the isolation of two nickel(III) complexes containing the macrocycle

(1) Abstracted in part from the Ph.D. thesis of E. I. Baucom, University of Illinois, Urbana, Ill., 1970.

(2) E. I. Baucom and R. S. Drago, *J. Amer. Chem. Soc.*, **93**, 6469 (1971).

(3) A. S. Foust and R. H. Soderberg, *ibid.*, **89**, 5507 (1967).

(4) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(5) A. Davidson, N. Edelstein, A. H. Maki, and P. H. Holm, *Inorg. Chem.*, **2**, 1227 (1963).

(6) A. L. Balch, F. Rohrscheid, and R. H. Holm, *J. Amer. Chem. Soc.*, **87**, 2301 (1965).

(7) R. S. Nyholm, *J. Chem. Soc.*, 2061 (1950); 2602 (1951); 2906 (1952); *Nature (London)*, **165**, 154 (1950).

(8) F. H. Burstall and R. S. Nyholm, *ibid.*, 3570 (1952).

(9) G. A. Barclay and R. S. Nyholm, *Chem. Ind. (London)*, 378 (1953).

(10) P. Kreisman, R. Marsh, J. R. Preer, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 1067 (1968).

(11) W. Klemm, W. Brandt, and R. Hoppe, *Z. Anorg. Allg. Chem.*, **308**, 179 (1961).

(12) N. F. Curtis and D. F. Cook, *Chem. Commun.*, 962 (1967).

5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet)—[Ni(tet)(NO$_3$)$_2$](HN$_2$O$_6$) and [Ni(tet)-SO$_4$]ClO$_4$·^{1}/$_3$H$_2$SO$_4$. Both compounds are stable as solids but decompose in solution. Similar macrocyclic ligands have led[13-15] to other claims of nickel(III) complexes.

The proposed six-coordinate nickel(III) complex NO$_2$[Ni(NO$_3$)$_4$] is something of an oddity in that the magnetic moment reported[16] was 4.54 BM, suggesting an essentially ionic complex with three unpaired spins.

The five-coordinate nickel(III) complexes reported are of two general types, trihalodiphosphines and haloglyoximates. The former were first reported by Jensen.[17,18] Like most nickel(III) complexes, tribromobis(triethylphosphine)nickel(III) decomposes in solution but is stable as a solid. The complex is formulated[18] as trigonal bipyramidal.

Wymore and Bailar[19] reported a similar complex, tribromotetraethylethylenediphosphinenickel(III), which had properties analogous to those of Jensen's compound (μ = 2.0 BM). Van Hecke and Horrocks[20] investigated the analogous tetraphenylethylene- and tetraphenylpropylenediphosphine tribromides of nickel(III) (μ = 2.02 and 1.93 BM, respectively). They observed broad symmetrical epr signals for polycrystalline samples at 80°K corresponding to g = 2.218 but could not resolve the expected anisotropy.

Meek, *et al.*,[21] isolated the complex tribromobis(dimethylphenylphosphine)nickel(III), a nonelectrolytic monomer with a magnetic moment of 2.17 BM at 296°K. Recrystallization from benzene–pentane yielded a crystalline material whose magnetic properties suggested a stoichiometric ratio of one nickel(II) molecule per two nickel(III) molecules. This structure was confirmed by X-ray analysis, which also proved the trigonal-bipyramidal geometry of the nickel(III) complex. Bond distances within the nickel(III) molecule were similar to those observed in the planar nickel(II) moiety. No epr signal was observed at 295 or 80°K. This was taken as evidence that the complex is nickel(III) rather than a cation-stabilized radical ligand since an anisotropic pattern with $\langle g \rangle$ near 2.0–2.1 would be expected for the latter.

Other nickel(III) complexes include porphyrin complexes[22,23] prepared in cyclic voltammetric studies. According to these studies, epr evidence supports the formation of both a nickel(III) species ($\langle g \rangle$ = 2.235) and a cation-stabilized radical ligand ($\langle g \rangle$ = 2.027). Neither was isolated. Olson and Vasilevskis,[24] however, have succeeded in isolating what they claimed is a series of nickel(III) complexes with macrocyclic ligands such as 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetra-

azacyclotetradecane (tet, *vide supra*) (μ_A ranged from 1.79 to 2.03 BM).

Bis(π-cyclopentadienyl)nickel(II) is easily oxidized[25,26] (μ = 1.75 ± 0.1 BM). Hawthorne and coworkers[27-30] succeeded in replacing both one and two π-cyclopentadienyl rings with π-(3)-1,2- and π-(3)-1,7-carbollyl systems, obtaining neutral and anionic nickel(III) complexes (μ = 1.74–1.99 BM). Unlike most nickel(III) complexes, these are not highly colored, appear to be stable in solution, and decompose only above 300°. Crystal structures show them to be "sandwich" complexes, with the nickel atom centered between the two parallel rings.[31-33]

Experimental Section

Instrumentation.—Nmr, infrared, and ultraviolet spectra were obtained as previously described.[2]

Electron paramagnetic resonance studies were carried out with a Varian V-4500-10A X-band epr spectrometer and a 9-in. magnet equipped with field modulation and control unit Model V4560 and console Model V-FR2503 with Fieldial. Diphenylpicrylhydrazyl (DPPH) attached to the outside of the sample tube with cellophane tape served as a standard. Polycrystalline samples and frozen solutions were held in 4-mm quartz tubes. Frozen solutions were prepared by completely dissolving a small amount of the solid in the appropriate solvent and immediately freezing the solution by immersion in liquid N$_2$. Low-temperature studies were carried out by placing the sample tube into a dewar flask kept filled with liquid N$_2$. Sample tubes were sealed and stabilized against bumping by covering the tops with a large quantity of wax.

Conductivity measurements were carried out with a standard Wheatstone bridge assembly equipped with an electron tube to detect the achievement of a null point. Standard conductivity cells with platinum electrodes were used.

Magnetic moments were measured at two field strengths at ambient temperatures with a Gouy balance of standard design. The calibrant was Hg[Co(SCN)$_4$]. The susceptibilities were field independent, and the reported magnetic moments were corrected for diamagnetic contributions using Pascal's constants.[34]

Syntheses. *syn-2-Benzoylpyridine Oxime*, **BPOH (1)**.—The

1
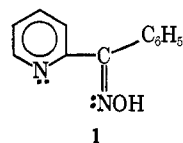
preparation is similar to that described by Trusell and Diehl;[35] however, our modifications seemed to produce a somewhat purer product. A solution of 68.2 g (0.372 mol) of 2-benzoylpyridine (Aldrich), recrystallized from ether–petroleum ether, in 125 ml of ethanol was treated with a solution of 51.3 g (0.73 mol) of NH$_2$OH·HCl and 34.1 g (0.853 mol) of NaOH in 130 ml of H$_2$O. The solution was refluxed 1.5 hr, cooled, and treated with powdered Dry Ice to pH 7. After filtration, washing with water, and air-drying, the crude oxime was stirred 15 min with 200 ml of ethanol–ether. The residue on filtration was

(13) N. F. Curtis, *Chem. Commun.*, 881 (1966).

(14) E. K. Barefield and D. H. Busch, *ibid.*, 522 (1970).

(15) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **8**, 1611 (1969).

(16) C. C. Addison and B. G. Ward, *Chem. Commun.*, 819 (1966).

(17) K. A. Jensen, *Z. Anorg. Allg. Chem.*, **229**, 265 (1936).

(18) K. A. Jensen, B. Nygaard, and K. T. Pedeygen, *Acta Chem. Scand.*, **17**, 1126 (1963).

(19) C. E. Wymore and J. C. Bailar, *J. Inorg. Nucl. Chem.*, **14**, 42 (1960).

(20) G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1968 (1966).

(21) D. W. Meek, E. C. Alyea, J. K. Stalick, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 4920 (1969).

(22) A. Wolberg and J. Manassen, *ibid.*, **92**, 2982 (1970).

(23) A. Wolberg and J. Manassen, *Inorg. Chem.*, **9**, 2365 (1970).

(24) D. C. Olson and J. Vasilevskis, *ibid.*, **8**, 1611 (1969).

(25) G. Wilkinson, P. L. Paulson, and F. A. Cotton, *J. Amer. Chem. Soc.*, **76**, 1970 (1954).

(26) F. Engelmann, *Z. Naturforsch. B*, **8**, 775 (1953).

(27) L. F. Warren, Jr., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **89**, 470 (1967).

(28) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879 (1968).

(29) R. J. Wilson, L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, **91**, 758 (1969).

(30) L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, **92**, 1157 (1970).

(31) B. G. DeBoer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **7**, 2288 (1968).

(32) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *ibid.*, **6**, 1911 (1967).

(33) C. B. Harris, *ibid.*, **7**, 1517 (1968).

(34) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960.

(35) F. Trusell and H. Diehl, *Anal. Chem.*, **31**, 1978 (1959).

thoroughly air-dried and then refluxed 20 min in 200 ml of CHCl₃. After hot filtration and cooling, very slightly pink crystals were obtained (mp 146–148°). Recrystallization from ethanol with Darco yielded pure white crystals melting at 163–164° (lit.[35] mp 151°). *Anal.* Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.09; N, 14.12. Found: C, 72.91; H, 5.10; N, 14.04.

syn-2-Phenacylpyridine Oxime, PPOH (2).—The preparation

2
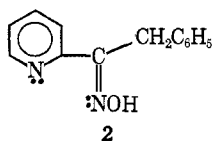
is based on the general preparation of pyridyl oximes reported by Nakashima.[36] Benzyl Grignard reagent was prepared in the standard manner with 5.83 g (0.24 g-atom) of Mg metal and 30.4 g (0.24 mol) of benzyl chloride in 300 ml of ether. To this solution at 0° was added dropwise a solution of 20.8 g (0.20 mol) of 2-cyanopyridine (distilled at 63–64° (30 mm)) in 50 ml of ether. After addition was complete, the mixture was stirred 0.5 hr at 0° and an additional 1.5 hr at room temperature. The mixture was treated with 500 ml of ice and 75 ml of 6 M H₂SO₄. The slurry was extracted with additional ether. All ethereal extractions were combined, washed with 5% aqueous Na₂CO₃, and dried over Na₂SO₄. The ether was removed under reduced pressure. The residual liquid was distilled and the fraction at 135–137° (30 mm) was collected.

The entire fraction was dissolved in ethanol and treated with an aqueous solution (30 ml) of 10.5 g (0.15 mol) of NH₂OH·HCl and 6.0 g (0.15 mol) of NaOH. The solution was warmed with stirring for 0.5 hr and then cooled overnight. The yield was 32.6 g (77% based on cyanopyridine) of crude product. Recrystallization from ethanol gave white crystals melting at 156° (lit.[36] mp 157°).

Bis(2-benzoylpyridine oximato)nickel(II), Ni(BPO)₂.—To a solution of 2.00 g (10.1 mmol) of 2-benzoylpyridine oxime and 0.55 g (10.2 mmol) of sodium methoxide in 20 ml of methanol was added a solution of 1.80 g (5.0 mmol) of Ni(ClO₄)₂·6H₂O in 20 ml of methanol. The bright red solution was evaporated to dryness under reduced pressure, and the residue was extracted several times with H₂O to remove NaClO₄ and excess reagents. The residue was dissolved in CHCl₃, extracted several times with H₂O, and dried over Na₂SO₄. The solvent was removed at reduced pressure at 0° yielding beautiful red crystals. *Anal.* Calcd for $C_{24}H_{18}N_4O_2Ni$: C, 63.62; H, 4.00; N, 12.37; Ni, 12.96. Found: C, 63.43; H, 3.98; N, 12.15; Ni, 12.40.

Tris(2-benzoylpyridine oximato)nickel(III), Ni(BPO)₃.—To a suspension of 1.28 g (7.0 mmol) of 2-benzoylpyridine oxime in 20 ml of 18 M aqueous NH₃ reagent acetone was added until all the oxime was dissolved. The solution was filtered and treated with a filtered solution of 0.48 g (2.0 mmol) of NiCl₂·6H₂O and 1.14 g (5.0 mmol) of (NH₄)₂S₂O₈ in 30 ml of H₂O. After standing 6–8 hr, the black crystals which had separated were removed by filtration, washed with H₂O, air-dried, washed with ether, and air-dried. The yield is 0.90 g (69%). The compound melts with decomposition at 177°, but the irregular shape of the crystals at the melting point indicates that some decomposition had occurred prior to melting. *Anal.* Calcd for $C_{36}H_{27}N_6O_3Ni$: C, 66.48; H, 4.19; N, 12.90; Ni, 9.01. Found: C, 66.20; H, 4.23; N, 12.75; Ni, 8.99.

Tris(2-phenacylpyridine oximato)nickel(III), Ni(PPO)₃.—The compound tris(2-phenacylpyridine oximato)nickel(III), Ni(PPO)₃, was prepared in the same manner as Ni(BPO)₃ except that less H₂O was used in the solution of the nickel(II) and oxidant, and the latter solution was added more slowly to prevent precipitation of the ligand. *Anal.* Calcd for $C_{39}H_{33}N_6O_3Ni$: C, 67.64; H, 4.80; N, 12.13; Ni, 8.48. Found: C, 67.50; H, 4.85; N, 12.04; Ni, 8.42.

Results and Discussion

Our isolation of a nickel(IV) complex with the anion of 2,6-diacetylpyridine dioxime (3) led us to attempt to develop a similar ligand which would stabilize a formal nickel(III) complex. The possibility of carrying out an epr study on this system would aid substantially

3
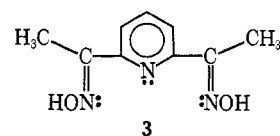
in product characterization. In view of the fact that neutrality often leads to insolubility in water when the water cannot coordinate to the complex, we chose 2-pyridine oximes as ligands likely to lead to isolatable nickel(III) complexes which would be stabilized in this oxidation state *via* their insolubility.

The black crystalline compound, Ni(BPO)₃, is moderately stable for several months in the absence of moisture and oxygen. It is soluble in most organic solvents but decomposes rather rapidly in solution at room temperature. Fresh solutions are essentially nonconducting, but on standing, decomposition of the complex occurs, giving rise to conducting species at a rate which parallels the change in color of the solution from dark green to yellow. Decomposition in nitromethane is first order in the complex, as measured by the increase in conductivity; the half-life at 25° is 28.5 min.

The electronic spectrum of the complex, measured as a mull at ambient temperature, exhibits only one clearly resolved transition, that at 13,850 cm⁻¹; at least six other transitions occur as broad overlapping bands. The transitions, in cm⁻¹, and relative intensities are 13,850 (8.35), 18,500 (6.3), 21,500 (7.9), 26,200 (10.4), 32,700 (17.4), and 41,100 (18.2).

Due to the instability of the complex in solution, no exact absorption coefficients could be measured; however, ϵ values on the order of 10^4 were estimated from the lowest energy transition of Ni(BPO)₃ in fresh acetone solutions. The solution spectra, like those of bis(diacetylpyridine dioximato)nickel(IV), Ni(DAPD)₂, were found to be highly solvent dependent. Strong hydrogen-bonding solvents gave spectra in which transitions occurred at much higher energy than in non-hydrogen-bonding solvents. As in the case of Ni(DAPD)₂, this dependence is taken as evidence of strong hydrogen bonding of the solvent to the oxime oxygens.

The instability of the complex in solution also prevented isolation of a diluted single crystal suitable for epr studies. However, a surprisingly sharp signal was observed for the undiluted polycrystalline material at room temperature. The epr spectrum illustrated in Figure 1 is a typical example of a polycrystalline solid with $S = \frac{1}{2}$.[37] From the three transitions, g_1, g_2, and g_3 are directly calculated to be 2.08, 2.10, and 2.14, respectively. It should be noted that no hyperfine structure was observed even though the half-width of the signal is sufficiently narrow ($\Delta H_{1/2} = 13$ G) to allow detection of splittings of about 5 G. (Since the expected pattern from three equivalent oxime nitrogens is 1:6:15:20:15:6:1, it is quite possible that even splittings of 2–3 G might be observed; the value 5 G is an upper limit of unresolved hyperfine.) Ideally, a complete calculation should be carried out to determine exact g values, line widths, and hyperfine splitting, but we were not interested in expending the considerable effort to calculate these parameters more accurately

(36) T. Nakashima, *Yakugaku Zasshi*, **77**, 1298 (1957).

(37) F. K. Kneubuhl, *J. Chem. Phys.*, **33**, 1074 (1960).
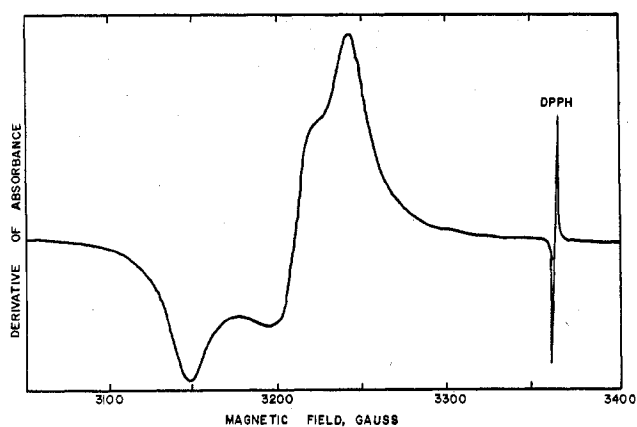
Figure 1.—Epr spectrum of polycrystalline Ni(BPO)$_3$.

for a rhombic system. The values reported are accurate enough for the qualitative nature of the application we intend to use them for. The magnetic moment of the complex is 1.75 ± 0.1 BM.

In Table I, the g values of Ni(BPO)$_3$ are compared

TABLE I

g VALUES OF OXIDIZED NICKEL COMPLEXES

	g_1	g_2	g_3	$\langle g \rangle$
Ni(diars)$_2$Cl$_2^+$ [a]	2.05	2.09	2.14	2.09
Ni[S$_2$C$_2$(CN)$_2$]$_2^-$ [b]	1.996	2.043	2.140	2.060
Ni(BDPH)$^+$ [c]				2.013
Ni(PDA)$_2^-$ [d]	1.990	2.006	2.102	2.033
Ni(gma)$_2^-$ [e]	1.978	2.005	2.026	2.003
Ni(BABH)$^+$ [f]				2.001
Ni(BPO)$_3$	2.08	2.10	2.14	2.11
Ni^{3+} in TiO$_2$ [g]	2.084	2.085	2.254	2.141

[a] Reference 13. diars = o-phenylenebis(dimethylarsine). [b] E. I. Stiefel, J. H. Waters, E. Billing, and H. B. Gray, *J. Amer. Chem. Soc.*, **87**, 3016 (1965). [c] O. A. Gansow, R. J. Olcott, and R. H. Holm, *J. Amer. Chem. Soc.*, **89**, 5470 (1967). BDPH^{2-} = butane-2,3-dione bis(2'-pyridylhydrazone). This is suggested to be a cation-stabilized free radical. [d] Reference 4. PDA^{2-} = o-phenylenediamine dianion. [e] Reference 4. gma^{2-} = glyoxal bis(2-mercaptoanil) dianion. [f] Reference 4. BABH^{2-} = biacetyl bis(benzoylhydrazone) dianion (a suggested cation-stabilized free radical). [g] H. J. Gerritsen and E. S. Sabinsky, *Phys. Rev.*, **125**, 1853 (1962).

with those of several nickel(II)-stabilized radical ligands and nickel(III) complexes. Obviously, there is no sharp delineation between the two designations, as g values over the entire range from 2.00 to 2.14 are observed. However, if we consider only those complexes containing second- and third-row donors, we see that generally values of $\langle g \rangle$ for the nickel(II)-stabilized radicals fall below 2.06. Uncomplexed ligand radicals containing second- and third-row donors are expected to exhibit $\langle g \rangle$ values near the free-electron value of 2.0023 since the donor atoms, on which the electron largely resides, have no orbital contributions to g. On complexation, orbital contributions arising from the nickel alter $\langle g \rangle$ slightly from its free-electron value. Thus, nickel(II)-stabilized radical ligands of oxygen and nitrogen donors exhibit $\langle g \rangle$ values very near 2.0023.

On the other hand, the complex ion Ni(diars)$_2$Cl$_2^+$ exhibits an unusually high $\langle g \rangle$ for a nickel(II)-stabilized radical because of the considerable orbital contributions to g of the arsenic donor itself. (The epr spectrum of the uncomplexed ligand is very similar to that of Ni(diars)$_2$Cl$_2^+$ and has Δg = 0.14.[13]) The highest

$\langle g \rangle$ value in Table I belongs to nickel(III) in TiO$_2$. It seems that the values $\langle g \rangle$ = 2.11 and Δg = 0.06 for Ni(BPO)$_3$ are consistent with the electron residing in a predominantly metal orbital, and in the continuum of nickel(III) *vs.* nickel(II)-stabilized radical complexes Ni(BPO)$_3$ is considered to border on the side of a nickel(III) complex rather than a nickel(II)-stabilized radical ligand.

The absence of observable nitrogen hyperfine is also consistent with the designation of the oxidation state as nickel(III). The hyperfine splitting of the oxime nitrogen in the free radical BPO· is about 31 G.[38] The reduction of this splitting below 5 G implies that the spin resides in a largely metal orbital. This contrasts markedly with Ni(diars)$_2$Cl$_2^+$ in which the arsenic hyperfine of 23 G shows the electron to be in a largely ligand orbital. More hyperfine information on our complex might be obtained by preparing the complex enriched with ^{61}Ni and observing the nickel hyperfine splitting. In a similar experiment Ni((C$_6$H$_5$)$_2$C$_2$S$_2$)$_2^-$ enriched with ^{61}Ni exhibited hyperfine splitting of 4.5 ± 1.0 G;[5] Ni(BPO)$_3$ should exhibit a considerably larger splitting which could easily be resolved.

Ni(BPO)$_3$ appears to be stable to further oxidation. There was no visual or chemical evidence of a more highly oxidized species when oxidation of Ni(BPO)$_3$ was attempted. [Ideally electrochemical evidence could be sought to support this claim, but the instability of the complex in solution (*vide supra*) discouraged us from attempting such a study.] The absence of higher oxidized species also supports the claim that the species contains nickel(III) and not oxidized ligands because, to our knowledge, all complexes previously claimed to contain nickel(II)-stabilized radical ligands are part of a series in which two oxidation states higher than that of the classical nickel(II)–ligand system exist.[13,4,39]

It is of interest to extend a proposal made earlier[2] to account for the stabilization of high oxidation states to the complexes reported here and to those described in the Introduction. According to our earlier model, the formation and stabilization of high oxidation states is favored by a ligand with (1) a high concentration of charge on the donor atom to lower the VSIP (raise the energy) of the metal orbitals in an MO description or to give rise to a large spherical component for the ligand field in a ligand field description and (2) very strong σ-donor properties to mix strongly with the metal orbitals to delocalize the positive charge associated with the electron removal from the complex. In our preferred description of the coordinate bond,[40] the former property corresponds to a ligand possessing a large E number and the latter a large C. It is not possible to measure E and C numbers for the ligands reported here but we will present arguments based on the above considerations which help predict the relative magnitudes of these properties. In this way, E and C are being employed as in the old hard–soft concept which we have shown to be incorrect.[40,41]

(38) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., Sect. B*, 86 (1966).

(39) O. A. Gansow, R. J. Olcott, and R. H. Holm, *J. Amer. Chem. Soc.*, **89**, 5470 (1967).

(40) R. S. Drago, G. C. Vogel, and T. Needham, *J. Amer. Chem. Soc.*, **93**, 6014 (1971).

(41) R. A. Kabler and R. S. Drago, submitted for publication.

The strong spherical component (a large E property) raises the energy of the entire d-orbital manifold in the lower oxidation state species making oxidation occur more readily. The strong σ-donor property (a large C property) leads to enhanced metal orbital–ligand mixing when the electron is removed. This delocalizes the increased positive charge over the whole complex. The C number should be such that the metal ion bears the majority, but not all, of the increased positive charge in order to label the species nickel(III). In the absence of appreciable σ-ligand donation, very large energies are needed to remove electrons because the full increase in positive charge must be borne by the metal. The resulting species are potent oxidizing agents, e.g., K_3NiF_6. In the subsequent discussion, it should be assumed throughout that we are referring to oxidation by air and other common laboratory oxidizing agents which produce complexes of moderate stability. Furthermore, it should be emphasized that the stability of species is a complicated phenomenon with lattice energy and solvation contributions often playing a marked role. We are not addressing this question with our model. We are merely saying, suppose an oxidized complex can be obtained, what are the guidelines for obtaining an oxidized metal as opposed to a cation-stabilized radical ligand?

It is possible that metal oxidation could occur with a ligand having a very large E property and low C, but this would be unusual since ligands with a large E generally have an appreciable C. When the ligand is characterized by a low E number and large C, oxidation of the ligand will occur as the metal ion d orbitals in the absence of a large spherical component will drop lower in energy than the ligand orbitals when an electron is removed. (This sort of hybrid molecular orbital–ligand field description is the most convenient way to represent what is happening to the AO energies that lead to the final MO's.) A ligand with a large C number usually corresponds to one that is easily oxidized. We feel that the low E property, large C property is characteristic[40] of the dithiolate and bis(dimethylarsine) ligands. If the metal ion orbitals are only slightly above the ligand filled orbitals in the low oxidation state complex (by virtue of a small ligand E number), the slight formal charge increase of the metal upon oxidation lowers the largely metal orbitals below those that are largely ligand and the ligand is oxidized. Thus, this model provides a complete continuum in which the electron being removed from the complex comes from a molecular orbital that is largely (more than 50%) metal, equal metal and ligand, and largely ligand. As the words "oxidation state" are defined in most freshman textbooks, both electrons in the bond are assigned to the most electronegative element, e.g., ClBr. Thus, the metal's oxidation state is increased in all of the cases where the electron came from an orbital that after oxidation is at least 50% metal. There is no inconsistency in an oxidation state description and a molecular orbital description.

As shown by molecular orbital calculations, most of the negative charge in $DAPD^{2-}$ is localized onto the oxime nitrogen and oxygen giving rise to an expected large E property for this ligand. It is also a good σ donor[2] so the positive charge resulting from the removal of one electron from $Ni(DAPD)^{2-}$ is delocalized

effectively enough that the essentially e_g orbitals of the intermediate nickel(III) species remain high in energy. (A full unit of positive charge on the metal would greatly lower the essentially metal orbital energies.) A second electron is then lost from the unstable nickel(III) intermediate as easily as the first electron from nickel(II), or more so. Consequently, no nickel(III) species is detected. The stronger metal–ligand interaction and more extensive delocalization of charge onto the ligand is accompanied by a shortening of the metal–ligand bond[42] and if, with $DAPD^{2-}$, this shortening is more considerable in going from our undetected nickel(III) to -(IV) than in going from nickel(II) to -(III) (recall e_g electrons are being removed), this would account for the fact that nickel(III) is not observed when the nickel(II) and -(IV) complexes of $DAPD^{2-}$ are mixed.

Our inability to prepare a IV oxidation state with the BPO^- ligand can be attributed to smaller expected E and C numbers for this ligand than for $DAPD^{2-}$. The effect of the ligands in $Ni(BPO)_3^-$ on the energy of the d manifold is less (it is assigned a smaller E property) than in the case of $Ni(DAPD)_2^{2-}$, where the total charge on the ligands is $4-$ compared with $3-$ in the $Ni(BPO)_3$ complex. The poorer σ-donor properties of BPO^- can be similarly rationalized. In $Ni(BPO)_3^-$, there are only three sets of high-energy σ^b orbitals largely based on the imine nitrogens, compared with four in $Ni(DAPD)_2^{2-}$, so $DAPD^{2-}$ is a better σ donor than BPO^-. Moreover, the anchoring effect of the tridentate $DAPD^{2-}$ forces the pyridine nitrogen into closer proximity to the metal in $Ni(DAPD)_2^{2-}$ than its analog in BPO^-. The net result of these effects is that the σ^b-donor orbitals of $DAPD^{2-}$ would be assigned a higher C number than those of BPO^-. As a result, the occupied σ^* orbitals of $Ni(DAPD)_2^{2-}$ have considerably less metal character than those of $Ni(BPO)_3^-$. In contrast to $Ni(DAPD)_2^{2-}$, removal of an electron from $Ni(BPO)_3^-$ from an orbital that is less delocalized causes a significant decrease in the higher energy essentially metal orbital that is already at a lower energy than in $Ni(DAPD)_2^{2-}$ because of the smaller E number. Consequently, further oxidation of $Ni(BPO)_3$ becomes difficult and this complex is obtained instead of $Ni(BPO)_3^+$. Stronger oxidizing agents would be expected to oxidize the ligand.

It should be pointed out that, in the absence of electrochemical studies, the existence of $Ni(BPO)_3^+$ cannot be disproven. Such a species might exist for a very short time and thus escape notice. However, the possible existence of this transitory species in no way affects our arguments, as its very instability would support the fact that BPO^- is not as effective as $DAPD^{2-}$ in stabilizing the IV oxidation state.

The purpose of preparing and isolating $Ni(PPO)_3$ was to illustrate that the presence of an extended π system such as that in BPO^- is not necessary for the stabilization of nickel(III). There is no evidence to suggest that an extended π system is or is not important in determining the ability of the ligand to stabilize nickel(III) or -(IV) in general.

The five-coordinate complexes[17,18,20,21] $Ni(Phos)Br_3$ constitute the only apparent exception to our model.

(42) G. D. Stucky and G. Sproul, submitted for publication.

However, it is possible that in these complexes the phosphorus got oxidized resulting in a high-spin nickel(II) five-coordinate complex. Then spin pairing of the essentially metal electron in d_{z^2} with that on the phosphorus would account for the experimental observation that no ligand esr was observed. *Via* resonance or in a three-center MO description (d_{z^2} and two phosphorus σ orbitals), the two phosphorus atoms become equivalent. The unpaired electron is in the near doubly degenerate set, $d_{z^2-y^2}$, d_{xy}, consistent with a higher than spin-only value of 2.1 BM for the complexes. These complexes simply constitute a case where esr does not provide a handle on the molecular orbitals of interest in the complex, because in the three-center MO description of the nickel(II) complex, the electron is in the antibonding mainly metal MO.

Whether the phosphine or metal got oxidized depends upon the metal coefficient in the bonding MO of the oxidized species. In view of the C property of the phosphines, we prefer to think that there is a substantial increase in the metal contribution to the bonding MO in the oxidized species. (Recall the nonbonding MO has a node at the metal for a true three-center description.) Consequently, we feel the antibonding MO in the complex from which the electron has been removed is composed slightly more of phosphorus than metal so the phosphorus has been oxidized, but this is just speculation on our part.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA 95616

Preparation and Reactions of Tetrakis(methyl isocyanide) Complexes of Divalent Nickel, Palladium, and Platinum

BY JOEL STEVEN MILLER AND ALAN L. BALCH*

The preparation of the planar complexes [(CH₃NC)₄M][PF₆]₂ (M = Ni, Pd, Pt) is reported. Reaction of bromine with the platinum complex yields [(CH₃NC)₃PtBr][PF₆]; with iodine no reaction occurs. Methylamine adds to (CH₃NC)₄M²⁺ (M = Pd, Pt) to yield {(CH₃NH)₂C}₄M²⁺. The structure and chemical inertness of these complexes, which are the first examples of transition metals coordinated solely by ligands of the resonance-stabilized "carbene" type, are discussed. The structures of the complexes obtained by the addition of hydroxylamine to (CH₃NC)₄Pt²⁺ are discussed. Reaction of chelating dithiols S₂C₂O₂²⁻ and S₂C₂(CN)₂²⁻ with (CH₃NC)₄M²⁺ (M = Pd, Pt) produces (CH₃NC)₂M(dithiol) *via* ligand substitution, whereas ethanethiol adds to (CH₃NC)₄Pt²⁺ to yield (CH₃NC)₂Pt{C(SC₂H₅)NHCH₃}₂²⁺. The complexes have been characterized by elemental analysis, conductivity, pmr spectra, and infrared spectra.

Introduction

The reactions of coordinated isocyanide ligands, especially their susceptibility to attack by a variety of protic nucleophiles including amines,[1] hydrazines,[2] alcohols,[1b,d,f-i] water,[1h,3] and thiols,[1h] have recently attracted widespread attention. The ligands obtained from these addition reactions may be formulated either as carbenes (with possible resonance stabilization) **1a** or as C-metal-substituted amidinium ions **1b** for X = NH (or the equivalent for X = O, or X = S). These ligands and the complexes containing them are generally characterized by a high degree of stability toward hydrolysis, atmospheric oxidation, and

1a, X = NH, O, S   **1b**
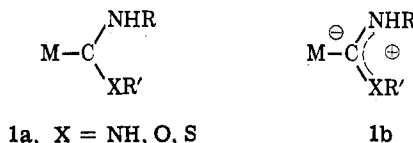
thermal decomposition. Frequently such ligands have been found to undergo reversible deprotonation. Although ligands of this type have only recently been satisfactorily characterized, the first preparation of a complex which has been demonstrated to contain this type of ligand was reported in 1925.[4] A number of early suggestions that such ligands might result from the reaction of nucleophiles with isocyanide complexes remain unconfirmed.[5] It also should be noted that ligands of type **1** are closely related to the resonance-stabilized carbene ligands found in complexes such as **2** which may be prepared from metal carbonyls.[6]

2
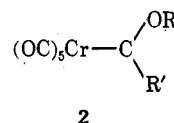
(1) (a) U. Schöllkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.,* **6**, 970 (1967); (b) E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sims, *Chem. Commun.,* 1322 (1969); E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc. A,* 21 (1971); (c) R. J. Angelici and L. M. Charley, *J. Organometal. Chem.,* **24**, 205 (1970); (d) F. Bonati and G. Minghetti, *ibid.,* **24**, 251 (1970); (e) F. Bonati, G. Minghetti, T. Boschi, and R. Crociani, *ibid.,* **25**, 255 (1970); (f) B. Crociani, T. Boschi, and U. Belluco, *Inorg. Chem.,* **9**, 2021 (1970); (g) E. M. Badley, B. J. L. Kilby, and R. L. Richards, *J. Organometal. Chem.,* **27**, C37 (1971); (h) W. J. Knebel and P. M. Treichel, *Chem. Commun.,* 516 (1971); (i) H. C. Clark and L. E. Manzer, *J. Organometal. Chem.,* **30**, C89 (1971); (j) J. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.,* **93**, 4613 (1971).

(2) (a) A. Burke, A. L. Balch, and J. H. Enemark, *ibid.,* **92**, 2555 (1970); (b) A. L. Balch and J. Miller, *ibid.,* **94**, 417 (1972); (c) W. M. Butler and J. H. Enemark, *Inorg. Chem.,* **10**, 2416 (1971); (d) W. M. Butler, J. H. Enemark, J. Parks, and A. L. Balch, submitted for publication; (e) G. Rouschias and B. L. Shaw, *J. Chem. Soc. A,* 2097 (1971).

(3) A. L. Balch and J. Miller, *J. Organometal. Chem.,* **32**, 263 (1971).

(4) L. Chugaev, M. Skanavy-Grigorieva, and A. Posniak, *Z. Anorg. Allg. Chem.,* **148**, 37 (1925).

(5) F. Hölzl, *Monatsh. Chem.,* **48**, 689 (1927); **51**, 1 (1930).

(6) E. O. Fischer and A. Massböl, *Angew. Chem., Int. Ed. Engl.,* **3**, 580 (1964).