the ethyl groups rather readily at the reaction temperature through the coordination of butadiene, and the ethyl groups play little role in the cyclotrimerization.

Cyclododecatriene is the main product when butadiene is oligomerized in the presence of the nickel catalyst without dipyridyl ligand, *e.g.*, nickel(0) cyclododecatriene complex.[2] This fact, together with the very slow rate observed in the present reaction, suggest that dipyridyl also plays little role in the selectivity of the reaction and exerts an inhibiting influence on the formation of the active catalyst species.

**Acknowledgment.** We are greatly indebted to Dr. Y. Fujiwara for the measurements of the nmr spectra and for the very helpful discussions.

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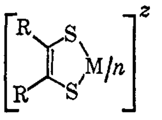
# Complete Electron-Transfer Series of the [M–N$_4$] Type

**Alan L. Balch**[1a] **and R. H. Holm**[1b]

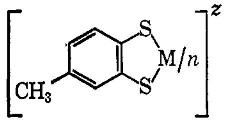
*Contribution from the Departments of Chemistry, Harvard University, Cambridge, Massachusetts, and the University of Wisconsin, Madison, Wisconsin.* *Received June 20, 1966*

**Abstract:** The existence of the electron-transfer series of the general type $[M–N_4]^z$ has been thoroughly investigated using the dianion of *o*-phenylenediamine as the basic ligand system and M = Co, Ni, Pd, and Pt. A five-membered series of bis chelate complexes is proposed in which the members have the net charges $z = -2, -1, 0, +1, +2$. The central ($z = 0$) member of the nickel series has been definitely established as the deep blue complex $Ni[C_6H_4(NH)_2]_2^0$, which was originally prepared by Feigl and Fürth from the oxidation of *o*-phenylenediamine in aqueous ammoniacal solution in the presence of nickel ion and air. By a similar route the complexes $M[C_6H_4(NH)_2]_2^0$, M = Co, Pd, Pt, have been synthesized and their structures established. Polarography in nonaqueous solvents has established the existence of the complete five-membered series for Ni, Pd, Pt, and the existence of the $z = -2, -1, 0, +1$ members for Co. Complexes with $z = -2, -1$ were not chemically prepared due to their oxidative instability. Epr studies of the $[M–N_4]^-$ species produced by controlled potential electrolysis reveal in glasses highly anisotropic *g* tensors (as observed in $[M–S_4]^-$ complexes), which serve to identify these species. In addition to the $[M–N_4]^0$ complexes, $[M–N_4]I$ salts were chemically prepared for M = Co, Ni, Pd, Pt. The paramagnetic cations of the Pd and Pt salts were shown to be the same as those generated electrochemically. The members with $z = +2$ have not as yet been synthesized. The previously prepared cation $Ni[(CH_3CNC_6H_5)_2]_2^{+2}$ has been shown to be the terminal oxidized member of an electron-transfer series with four detectable members, $z = +2, 0, -1, -2$. The $z = 0$ member has been prepared chemically. A qualitative explanation of the oxidative stability trend of $Ni[C_6H_4XY]_2^z$, in which X and Y represent various donor atom sets, is presented.

In a preceding paper[2] we have briefly summarized the current body of evidence which shows that the sulfur-bonded complexes **1** and **2** are members of a series of complexes which are interrelated by one-electron transfer reactions. It is now well recognized that members of a given series may usually be detected by polarographic measurements and frequently isolated, provided half-wave potentials lie in a range which makes isolation practicable. Limiting consideration to bis complexes ($n$ = 2), electron-transfer series of the $[M–S_4]^z$ type have been restricted to the $z = -2, -1, 0$ members, which are the only ones thus far isolated for any given series.[3]

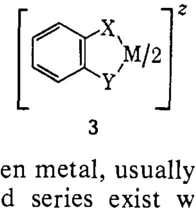


**1**



**2**

We have previously raised the question concerning the scope of such electron-transfer series in our studies of the four-coordinate complexes of general type **3**.[2,4] This question of scope actually consists of two parts: (i) what structural feature or features are necessary such that complexes exhibit oxidation–reduction propensity?; (ii) once an oxidation–reduction relationship between two complexes has been established, thereby defining a "series" of at least two members, what is the total number of members of that series which can be reasonably anticipated? We have attempted to effect a partial clarification of i by showing that with a given metal, usually nickel, at least two- or three-membered series exist with X = Y = O; X = Y = NH; X = NH, Y = S; X = O, Y = S.[4] The $z = -2$ and $-1$ members of X = Y = S series (specifically **2**) have now been firmly established[5] and the $z = 0$ member with M = Ni claimed.[6] In addition, a relevant suggestion concerning an electronic struc-



**3**

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[1] (a) National Science Foundation Predoctoral Fellow 1963–1966; (b) Alfred P. Sloan Foundation Fellow 1964–1967.

[2] F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966).

[3] The apparent $z = +1$ member of the series $[NiS_4C_4Ph_4]^z$ has been detected polarographically in dichloromethane solution (A. L. Balch and R. H. Holm, unpublished work).

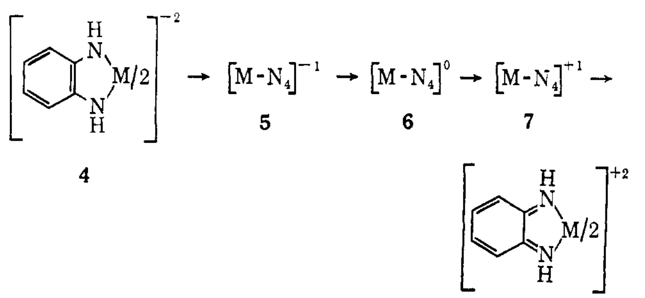
[4] A. L. Balch, F. Röhrscheid, and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2301 (1965).

[5] R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966).

[6] E. I. Steifel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965).

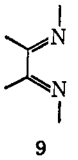
tural feature of the ligand system necessary to promote oxidation–reduction behavior has been offered.[7]

In this paper the results of efforts directed toward an elucidation of question ii are presented in the form of a detailed study of the complexes 3 with X = Y = NH. The ideas and methods of procedure rather closely parallel those of our recent, detailed study of complexes having X = Y = O.[2] By strict analogy we define the *complete* electron-transfer series for the complexes represented as $[\mathrm{M{-}N_4}]^z$ to consist of the five members **4**–**8**. The terminal reduced (**4**) and oxidized (**8**) members of the series are formulated to contain M(II) and the dianion of *o*-phenylenediamine, and M(II) and *o*-benzoquinonediimine, respectively. The potentially stable limits of the series are then defined by terminal reduced and oxidized forms of the $o$-$\mathrm{C_6H_4(NH)_2}$ ligand system in combination with a stable valence state of the metals employed. Simple or complex salts of $o$-$\mathrm{C_6H_4(NH)_2}^{-2}$ have not been reported. *o*-Benzoquinonediimine has been prepared in solution[8] but has not been isolated. Nonetheless, it does not appear unreasonable to conceive of the existence of these entities in stabilizing combination with appropriate metal ions.



**4** **5** **6** **7** **8**

A number of published reports, in addition to analogy with $[\mathrm{M{-}S_4}]^z$ series, have provided stimulus for investigation of the potential series **4**–**8**. First and most important, Feigl and Fürth[9] have isolated from the reaction of $\mathrm{Ni^{+2}}$ and *o*-phenylenediamine in aqueous ammonia in the presence of air a deep blue compound for which they claimed the formulation $\mathrm{Ni(C_6H_6N_2)_2}$. The empirical formula was subsequently questioned by Bardoděj[10] (*vide infra*), who put forth a revised structure and isolated the corresponding palladium complex. The Feigl–Fürth formulation implies that their complex is the intermediate member **6** of the electron transfer series. Second, there is a considerable body of literature describing isolation and characterization of bis and tris complexes containing alone or in resonance combination an $\alpha$-diimine unit **9** as part of the chelate ring structure. Complexes of



**9**

*o*-phenanthroline, 2,2′-bipyridyl, and glyoximes are well recognized. Of especial relevance are complexes of simple $\alpha$-diimines,[11–17] which lend credence to the supposition that complexes of type **8** can exist. There is no published information suggestive of the existence of the other members of the series **4**, **5**, and **7**, or of complexes structurally related thereto.

Our previous work has demonstrated that the well-defined electron transfer properties of $[\mathrm{M{-}S_4}]$ complexes **1**, leading in all cases to a two- or three-membered series, do not extend beyond two-membered series for the $[\mathrm{M{-}O_4}]$ complexes **3**.[2] Herein are presented results of our investigation of the related $[\mathrm{M{-}N_4}]$ complexes, which show exceptionally well-developed electron transfer properties. The existence of four- and five-membered series for several coordinated metals has been demonstrated.

## Experimental Section

**Preparation of Compounds.** Practical grade *o*-phenylenediamine was used without further purification unless otherwise stated. Purification was achieved by recrystallization from water containing potassium dithionate to retard oxidation. Biacetylbisanil and biacetylbisanilnickel(II) dinitrate were prepared according to the procedure of Bähr and Kretzer.[12]

**$\mathrm{Ni[C_6H_4(NH)_2]_2}$. Method 1.** A solution of 10 g of nickel chloride hexahydrate in 30 ml of water and 30 ml of concentrated aqueous ammonia was added to a solution of 6 g of *o*-phenylenediamine in 800 ml of warm water. This mixture was stirred in an open beaker for 24 hr. A deep blue precipitate formed and was collected by filtration, washed with water and acetone, and dried. The yield of this crude material was ~70%. Purification was accomplished by continuous infusion–extraction into acetone. The first extracts of a greenish color were discarded. Once a deep blue extract was obtained, the extraction was allowed to proceed for several days. Fine crystals, ranging in surface color from deep blue to a metallic greenish gold, formed during the extraction. These were collected, washed with acetone, and vacuum dried.

*Anal.* Calcd: C, 53.19; H, 4.46; N, 20.68; Ni, 21.66. Found: C, 53.17; H, 4.54; N, 20.42; Ni, 21.78.

**Method 2.** A solution of 5 g of purified *o*-phenylenediamine in 600 ml of ether at 0° was passed through a column containing 30 g of $\mathrm{PbO_2}$. The red effluent solution was led under a nitrogen atmosphere into a solution of 3 ml of nickel carbonyl in 75 ml of ether. This mixture was allowed to stand for 12 hr while a deep blue precipitate formed and gas slowly evolved. The solid was collected by filtration, washed with ether, and purified by extraction as in the first preparation.

*Anal.* Found: C, 52.69; H, 4.47; N, 20.80.

**$\mathrm{Pd[C_6H_4(NH)_2]_2}$.** A solution of 1.8 g of *o*-phenylenediamine in 200 ml of warm water was added to a solution of 1.0 g of palladium chloride and 1.0 g of potassium chloride in 800 ml of water. The pH was adjusted to 9 by the addition of aqueous ammonia and kept at that value while the solution was stirred in an open beaker for 12 hr. The resultant deep blue precipitate was collected, washed with water and acetone, and dried. The crude yield was variable, running from 0.5 to 1.6 g (28–90%). Purification was accomplished by extraction into acetone. The green extracts were discarded. After several days of extraction fine red crystals formed from the blue solution. These were collected, washed with acetone, and vacuum dried. Grinding these red crystals gives a deep blue powder; solutions prepared from them are also intensely blue.

*Anal.* Calcd: C, 45.23; H, 3.80; N, 17.58. Found: C, 45.59; H, 4.17; N, 17.71.

**$\mathrm{Pt[C_6H_4(NH)_2]_2}$.** A solution of 1 g of *o*-phenylenediamine dissolved in 200 ml of water was added to 300 ml of an aqueous solution containing 1 g of potassium tetrachloroplatinite. The pH was adjusted to 10 by the addition of aqueous ammonia. After stirring for 12 hr in an open beaker, the violet product (0.9 g, 91%) was collected by filtration, washed with water and acetone, and dried. Purification was achieved in the same manner as for the nickel

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[7] B. G. Werden, E. Billig, and H. B. Gray, *Inorg. Chem.*, **5**, 78 (1966).

[8] R. Willstätter and A. Pfannenstiel, *Ber.*, **38**, 2348 (1905).

[9] F. Feigl and M. Fürth, *Monatsh.*, **48**, 445 (1927).

[10] Z. Bardoděj, *Collection Czech. Chem. Commun.*, 20, 176 (1955).

[11] G. Bähr, *Z. Anorg. Allgem. Chem.*, **267**, 137 (1951).

[12] G. Bähr and A. Kretzer, *ibid.*, **267**, 161 (1951).

[13] P. Krumholz, *J. Am. Chem. Soc.*, **75**, 2163 (1953).

[14] D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 1137 (1956).

[15] R. C. Stoufer and D. H. Busch, *ibid.*, **78**, 6016 (1956).

[16] P. E. Figgins and D. H. Busch, *ibid.*, **82**, 820 (1960).

[17] M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963).

and palladium analogs. The final product is obtained as fine crystals with a blue or metallic green sheen which dissolve to give deep blue solutions.

*Anal.* Calcd: C, 35.38; H, 2.97; N, 13.75. Found: C, 35.07; H, 2.71; N, 13.79.

**$Co[C_6H_4(NH)_2]_2$.** Ten grams of cobalt chloride hexahydrate dissolved in 200 ml of water and 50 ml of concentrated aqueous ammonia were oxidized by a stream of air. A solution of 10 g of *o*-phenylenediamine in 400 ml of warm water was added after oxidation was complete. A deep violet solid which formed during 2 hr of stirring in an open beaker was collected, washed with water and acetone, and dried. Purification was achieved by continuous extraction into acetone; the first green extracts were discarded. During several days, black-violet crystals formed in the violet extraction solution. These were collected, washed with acetone, and dried. To obtain an analytical sample, a second extraction under anaerobic conditions was required since this complex is slowly decomposed by air in solution. The crystalline solid does not appear to be affected by atmospheric oxygen over a period of 18 months.

*Anal.* Calcd: C, 53.15; H, 4.46; N, 20.66. Found: C, 53.24; H, 4.83; N, 20.57.

**$Ni[4\text{-}i\text{-}C_3H_7C_6H_4(NH)_2]_2$.** A more soluble neutral complex was sought for certain solution measurements. The complex formed from 4-isopropyl-*o*-phenylenediamine[18] partially satisfies this requirement. A solution of 1.65 g of nickel chloride hexahydrate in 50 ml of water was added to 1.2 g of 4-isopropyl-*o*-phenylenediamine dihydrochloride dissolved in 50 ml of water. Aqueous ammonia (10 ml) was added and this mixture stirred in an open beaker for 24 hr. The resulting blue solid was collected, washed with water, and vacuum dried. After three recrystallizations from dichloromethane the final product was obtained as deep blue crystals.

*Anal.* Calcd: C, 60.88; H, 6.81; N, 15.78. Found: C, 61.18; H, 6.76; N, 14.96.

**$M[C_6H_4(NH_2)]_2I$ (M = Ni, Pd, Pt).** These salts were obtained from the reaction of 1 equiv of iodine with a mole of the neutral complex. The preparation of the platinum compound is given as a typical example. Essentially quantitative yields were obtained in all cases. The final products are all dark powders which are slightly soluble in dimethyl sulfoxide and N,N-dimethylformamide to give green solutions.

**$Pt[C_6H_4(NH)_2]_2I$.** A solution of 0.1177 g (0.928 mg-atom) of iodine in 70 ml of acetone was added over a period of 2 hr to a slurry of 0.3753 g (0.921 mmole) of $Pt[C_6H_4(NH)_2]_2$ in 30 ml of acetone. The crystals of $Pt[C_6H_4(NH)_2]_2$ were slowly transformed into a brown-black powder which was collected by filtration and washed with acetone after the reaction mixture stood with occasional stirring for 12 hr.

*Anal.* Calcd for M = Pt: C, 26.98; H, 2.26; N, 10.49. Found: C, 26.68; H, 2.23; N, 9.93. Calcd for M = Ni: C, 36.23; H, 3.04; N, 14.08. Found: C, 36.18; H, 3.43; N, 13.92. Calcd for M = Pd: C, 32.38; H, 2.72; N, 12.58. Found: C, 31.75; H, 2.92; N, 12.83.

**$Co[C_6H_4(NH)_2]_2I$.** A solution of 0.432 g (3.40 mg-atoms) of iodine in 50 ml of acetone was added slowly to a slurry of 0.907 g (3.32 mg-atoms) of $Co[C_6H_4(NH)_2]_2$ in 25 ml of acetone. After 6 hr of standing with occasional stirring, the solution was filtered to collect a black solid, which was washed with acetone and dried. An analytical sample was obtained by extraction into acetonitrile. The product was obtained as green crystals which give a blue solution.

*Anal.* Calcd: C, 36.21; H, 3.04; N, 14.07. Found: C, 35.99; H, 3.70; N, 13.64.

**$Ni[(CH_3CNC_6H_5)_2]_2$.** This compound is extremely oxygen sensitive and precautions must be taken to work under a nitrogen atmosphere and in oxygen-free solvents. Nickel carbonyl (3 ml) was added to a solution of 10 g of biacetylbisanil in a mixture of 125 ml of benzene and 200 ml of *n*-pentane. The solution was heated to a very gentle reflux for 6 hr while gas was evolved, and a deep violet color developed. The solution was then cooled to room temperature and stirred for 18 hr. The black crystalline product (5 g, 45%) was collected and vacuum dried. Extraction into 4:1 pentane-dichloromethane mixture has proven to be a feasible means of purification on a large scale. However, a slightly purer product in the form of shiny black crystals is obtained by recrystallizing 1 g of crude complex from 300 ml of toluene and 75 ml of acetone.

*Anal.* Calcd: C, 72.33; H, 6.07; N, 10.54. Found: C, 72.03; H, 6.06; N, 10.29.

**$Ni[(CH_3CNC_6H_5)_2]_2I_2$.** A solution of 3.0 g (7.1 mmoles) of nickel iodide hexahydrate in 75 ml of acetone was added to a solution of 3.4 g (14 mmoles) of biacetylbisanil in 75 ml of acetone. The orange crystalline powder which rapidly precipitated was collected, washed with acetone, and dried. Extraction into acetone yielded the purified complex as red-orange crystals. After collection and washing with acetone, the crystals were dried under vacuum at 80° over $P_2O_5$. Dark red-brown crystals result.

*Anal.* Calcd: C, 48.95; H, 4.11; N, 7.14. Found: C, 48.78; H, 4.17; N, 7.23.

$NiC_{12}H_{12}N_4I_2$. A solution of 0.624 g (4.92 mg-atoms) of iodine in 70 ml of peroxide-free tetrahydrofuran was added slowly to a slurry of 0.665 g (2.45 mmoles) of $Ni[C_6H_4(NH)_2]_2$ in 70 ml of peroxide-free tetrahydrofuran. After 8 hr of stirring, the original blue crystals were transformed into a gray-green powder which was collected, washed with tetrahydrofuran, and vacuum dried.

*Anal.* Calcd: C, 27.46; H, 2.31; N, 10.68. Found: C, 27.31; H, 2.36; N, 10.65.

**Physical Measurements.** Polarographic data were obtained by using an ORNL Model 1988 polarograph equipped with three-electrode geometry. Additional experimental details are given in footnotes to Table III. Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Magnetic susceptibilities were measured by the Gouy method using an aqueous nickel chloride solution as the calibrant. Conductivities were determined by use of a Serfass conductivity bridge. Infrared spectra of solids were measured on a Cary-White Model 16 spectrometer; a Perkin-Elmer 421 spectrometer was used for solution measurements. Mass spectra were recorded on a Picker MS-9 spectrometer using 70-ev ionizing electrons. A Varian Model V-4502 spectrometer was employed for the esr measurements. Hyperfine splittings and *g* values were determined using the dual cavity method and the same reference complexes as in previous work.[2] Certain of the paramagnetic species were generated by controlled-potential electrolysis at a thin platinum wire electrode within a 3-mm glass sample tube. This tube was placed within the epr cavity and its temperature regulated by the Varian temperature control. After the spectrum of the paramagnetic species was measured in solution at room temperature, the *g* value anisotropy was obtained by continuing the electrolysis until the species could be visually detected along the entire length (~3 cm) of the platinum wire. The sample was then cooled to ~100°K in order to form a glass and the resonance signals measured. A 3:1 v/v dimethylformamide-acetone solvent was employed; this solvent gives a sufficiently conducting medium for purposes of electrolysis and forms a transparent glass at ~100°K. The accuracy of *g* values given in Table IV is at least ±0.001 for solutions, ±0.002 for glasses, and ±0.005 for polycrystalline samples, unless otherwise indicated in the table.

**Table I.** Conductivity and Magnetic Susceptibility Data

| Compound | Λ, cm² mole⁻¹ ohm⁻¹ [a] | $\mu_{eff}$, BM[b] |
|---|---|---|
| $Ni[C_6H_4(NH)_2]_2^0$ | 0 | Diamagnetic |
| $Pd[C_6H_4(NH)_2]_2^0$ | 0 | Diamagnetic |
| $Pt[C_6H_4(NH)_2]_2^0$ | 0 | Diamagnetic |
| $Co[C_6H_4(NH)_2]_2^0$ | 0 | 2.20 |
| $Ni[C_6H_4(NH)_2]_2I$ | 33[c] | 1.18 |
| $Pd[C_6H_4(NH)_2]_2I$ | 25 | *d* |
| $Pt[C_6H_4(NH)_2]_2I$ | 28 | *d* |
| $Co[C_6H_4(NH)_2]_2I$ | 24 | Diamagnetic |
| $Ni[C_6H_4(NH)_2]_2I_2$ | ... | Diamagnetic |
| $Ni[(CH_3CNC_6H_5)_2]_2^0$ | ... | Diamagnetic |
| $Ni[(CH_3CNC_6H_5)_2]_2I_2$ | 253[e] | 3.02 |
| $Ni[(CH_3CNC_6H_5)_2]_2(NO_3)_2$ | 245[e] | 3.12 |
| $Ni[(CH_3CNCH_3)_2]_3I_2$[f] | 322[e] | ... |

[a] Measured in ~$10^{-3}$ *M* DMSO solution unless otherwise stated. In DMSO 1:1 electrolytes have conductivities in the range 24–42 cm² mole⁻¹ ohm⁻¹ (P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956)). [b] Data refer to solids at ~ 25°; diamagnetic susceptibilities not accurately measured. [c] Compound unstable in DMSO; measurement made immediately after solution prepared. [d] Insufficient sample for accurate measurement. [e] In ~$10^{-3}$ *M* acetonitrile solution. [f] Reference compound for conductivity of 1:2 complex iodide salt in acetonitrile; prepared according to ref 16.

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[18] R. L. Clark and A. A. Pessolano, *J. Am. Chem. Soc.*, **80**, 1657 1958).

**Table II.** Electronic Spectra of $M[C_6H_4(NH)_2]_2^0$ [a]

| | |
|---|---|
| $Ni[C_6H_4(NH)_2]_2^0$ | 7900 (54,900), 6500 (5640), 5600 sh (2140), 5200 (1560), 4200 sh (1260), 4000 (1160), 3350 (4210), 3100 sh (4670), 2760 (9040) |
| $Pd[C_6H_4(NH)_2]_2^0$ | 7800 (48,200), 6210 (1700), 5680 (1280), 5110 (1130), 4580 (924), 3500 (3870), 3110 (5520), 2760 (7430) |
| $Pt[C_6H_4(NH)_2]_2^0$ | 7820 (3310), 7500 sh (8950), 7110 (96,700), 6950 (69,900), 6800 sh (52,200), 6500 sh (12,900), 5970 (3270), 5650 (3710), 5450 (3180), 5250 (2420), 4770 (1680), 3650 (1150), 3280 (4390) |
| $Co[C_6H_4(NH)_2]_2^0$ | 11,350 (3840), 7630 (11,700), 5880 (17,700), 4200 (2730), 3370 (4640) |

[a] Spectra measured in DMSO solution; maxima or shoulders (sh) given in A; molar extinction coefficients are in parentheses.

## Results and Discussion

In the sections which follow evidence is presented for the existence of some or all of the members of the electron transfer series **4**–**8** with different coordinated metals. Results of relevant physical measurements are given in Tables I–IV and Figures 1–3.

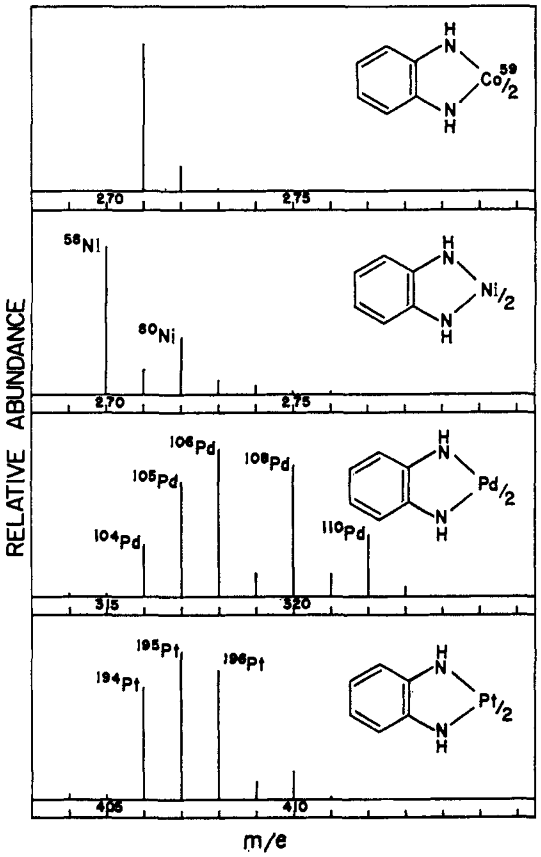


Figure 1. Mass spectral results in the parent ion mass region of $M[C_6H_4(NH)_2]_2^0$ complexes.

**Synthesis and Characterization of $M[C_6H_4(NH)_2]_2^0$ Complexes.** By reaction of the appropriate metal salt with *o*-phenylenediamine in aqueous ammoniacal solution in the presence of air the previously reported nickel[9] and palladium[10] complexes were reprepared and the new cobalt and platinum analogs isolated. Similar reactions with Cu(II), Zn(II), Fe(II), Mn(II), and Ag(I) failed to yield corresponding complexes. Bardoděj was unable to prepare a copper complex, and also cobalt and platinum complexes, which we have isolated. All four neutral complexes are intensely colored in the solid and solution phases. Their extremely low solubility rendered purification difficult and an extraction method, which yielded ~10–50 mg of pure product per day, was employed. Of common solvents tested the complexes appear most soluble in DMSO, DMF, pyridine, and acetone. The electronic spectra of these complexes are extremely rich, as can be seen from the data in Table II. These data were obtained from solutions prepared from high-purity samples and should be useful to others in assessing the purity of these complexes in any subsequent preparations.

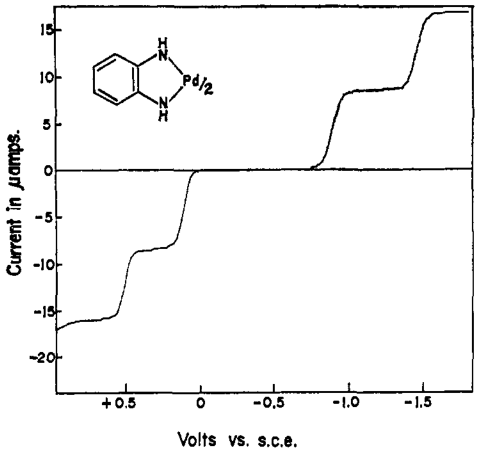


Figure 2. Polarographic waves arising from the oxidation and reduction of $Pd[C_6H_4(NH)_2]_2^0$ in dimethyl sulfoxide solution.

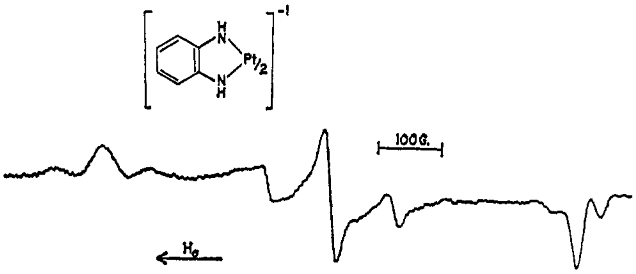
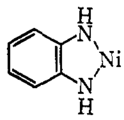
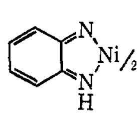
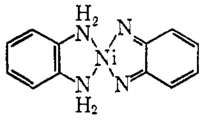


Figure 3. Epr spectrum of the one-electron reduction product of $Pt[C_6H_4(NH)_2]_2^0$ produced in dimethylformamide–acetone solution (3:1, v/v) by controlled potential electrolysis.

Of prime importance is the establishment of the structures of the neutral complexes. Feigl and Fürth[9] proposed the structure **10** for the nickel complex, which if correct would strongly imply that this complex is the intermediate member **6** of the electron transfer series for nickel, and should then be oxidizable and reducible. Bardoděj[10] rejected **10** in favor of **11**. Nyholm[19a] also did not accept **10** and considered forms which contain coordinated amino groups, such as **12**. The distinguishing feature of these structures is the


**10**


**11**


**12**

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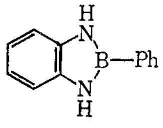
(19) (a) R. S. Nyholm, *Chem. Rev.*, **53**, 263 (1953); (b) E. Nyilas and A. H. Soloway, *J. Am. Chem. Soc.*, **81**, 2681 (1959).

number and distribution of hydrogen atoms bonded to the four donor nitrogens.

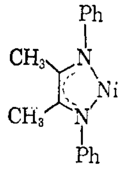
The infrared spectra of the crystalline neutral complexes of Co, Ni, Pd, and Pt are nearly identical in the 3500–1400-$cm^{-1}$ region. All exhibit a triplet of N–H stretches in the 3280–3320-$cm^{-1}$ region. 2-Phenylborobenzimidazoline[19b] (**13**) shows two N–H bands (3417, 3440 $cm^{-1}$) in the solid. However, **13** and the soluble $Ni[4\text{-}i\text{-}PrC_6H_3(NH)_2]_2^0$ in dichloroethylene solution show single sharp N–H stretches at 3475 and 3367 $cm^{-1}$, respectively, proving that the multiple bands in the crystal are due to solid state effects. The solution spectra are consistent only with the presence of NH groups,[20] thereby eliminating **12**, but do not distinguish between **10** and **11**.



**13**

The mass spectra of the neutral complexes offers persuasive evidence in all cases for the ligand structure shown in **10**. For each complex the ion of highest *m/e* observed corresponds to the parent ion of formula $MC_{12}H_{12}N_4^+$, and not $MC_{12}H_{10}N_4^+$. Mass spectral results in the parent ion region of each complex are given in Figure 1. The peaks of major intensity correspond to metal isotopes with large abundances and the entire pattern of intensities observed at various values of *m/e* in the parent ion region is in good agreement with that expected on the basis of relative isotopic abundances. In each case a molecular ion was observed at *m/e* corresponding to $MC_6H_6N_2^+$; this observation lends support to the formulation **10** in which both ligands are equivalent. An ion of weaker intensity with *m/e* corresponding to $MC_{12}H_{12}N_4^{+2}$ was also detected for each complex. These species are easily distinguished despite their lower intensity because the presence of a number of metal isotopes of odd mass require that some half-integral *m/e* values be observed for the doubly charged ions.

The establishment of the correct structure of the neutral nickel complex suggests an alternative method of preparation of this complex and the preparation of another $[Ni\text{–}N_4]^0$ complex of different ligand structure. The reactions employed are analogous to that of $Ni(CO)_4$ and other metal carbonyls with bistrifluoromethyl-1,2-dithietene, which yield $[M\text{–}S_4]^0$ complexes.[21] By this analogy the extreme oxidized form of the ligand, *i.e.*, an α-diimine, should react with $Ni(CO)_4$ to yield neutral bischelate species. Although *o*-benzoquinonediimine has never been isolated it is believed to be the initial, albeit transient, product of the reaction of *o*-phenylenediamine with lead dioxide.[8] Ether solutions supposedly containing this compound do indeed react with $Ni(CO)_4$ to yield a product identical in every respect with that from the Feigl–Fürth reaction which, therefore, must be **10**. This reaction has been extended to include one of the few stable, isolable α-diimines known, biacetylbisanil.[12] This compound reacts with $Ni(CO)_4$ to yield the deep blue, very air-unstable complex **14**, whose color and diamagnetism support its analogy to **10**. This analogy is further strengthened by the oxidation–reduction properties of **14** which to a considerable degree parallel those of **10** (*vide infra*).



**14**

The $[M\text{–}N_4]^0$ complexes of nickel, palladium, and platinum are all nonelectrolytes and diamagnetic (*cf.* Table I) as are all known $[M\text{–}S_4]^0$ species containing the same metals. The magnetic moment of the cobalt complex indicates a doublet ground state and a monomeric structure in the crystalline solid. In this respect the complex is unlike the only known $[Co\text{–}S_4]^0$ complex, $[CoS_4C_4(CF_3)_4]_2$ (structure **1**), which is dimeric and diamagnetic in both the solution and the solid.[22] However, like $[CoS_4C_4(CF_3)_4]_2$[21,23] this complex does undergo well-defined electron-transfer reactions (*vide infra*).

**Polarographic Evidence for the Electron-Transfer Series.** Confirmation of the proposed five-membered electron-transfer series **4–8** is supplied by the polarographic data set out in Table III. For each of the complexes $M[C_6H_4(NH)_2]_2$, M = Ni, Pd, Pt, polarographic waves are observed which link the $[M\text{–}N_4]^{+2}$ to the $[M\text{–}N_4]^{-2}$ member by a series of reversible one-electron reactions. *No other waves are observed.* The same observation is made for the $Ni[(CH_3CNC_6H_5)_2]_2^z$ series, whose $z = 0$ member is **14**. Here it is particularly relevant to observe that after the last electrode reaction (at −0.61 v) in the direction of increasing positive applied potential, no other waves are evident despite the large remaining anodic region (to +1.0 v) accessible in acetonitrile. This same observation has been made in dichloromethane solution when an anodic range to at least +3.0 v, relative to the reference half-cell used,[2] exists.

In Figure 2 a typical polarogram obtained in a solution of $Pd[C_6H_4(NH)_2]_2^0$ is reproduced. The four one-electron waves which interconnect the five members of the $[Pd\text{–}N_4]^z$ series are clearly observed. Solutions of the platinum analog give rise to equally well-developed waves at somewhat different potentials. It is to be noted that from slope and $i_d/C$ data (Table III), one-electron processes in DMSO solution at both a dropping mercury electrode and a platinum electrode are confirmed. Moreover, polarography of the monoiodide salts, $M[C_6H_4(NH)_2]_2I$, M = Pd, Pt (described below) reveals that the cations are reducible to the $z = 0, -1, -2$ members at half-wave potentials which are within ±20 mv of the values reported in Table III.[24] Polarographic oxidation of these salts

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[20] Nyholm[19a] has concluded on the basis of undocumental infrared evidence that amino groups were absent. Coordinated NH groups in bis(oxamido)metal(II) complexes exhibit in the solid phases a single N–H stretch at 3310–3315 $cm^{-1}$ (P. X. Armendarez and K. Nakamoto, *Inorg. Chem.*, **5**, 796 (1966)). Differentiation between coordinated NH and $NH_2$ groups by infrared spectra in complexes derived from *o*-aminobenzenethiol has recently been claimed (L. F. Larkworthy, J. M. Murphy, and D. J. Phillips, *J. Am. Chem. Soc.*, **88**, 1570 (1966)).

[21] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

[22] J. H. Enemark and W. N. Lipscomb, *ibid.*, **4**, 1729 (1965).

[23] A. L. Balch and R. H. Holm, *Chem. Commun.*, 552 (1966).

[24] There is a single exception in these six reductions. The +1 → 0 reduction of $[Pt\text{–}N_4]I$ occurs at a potential 0.09 v more cathodic than the corresponding oxidation of the $[Pt\text{–}N_4]^0$ complex. The cause of this

**Table III.** Polarographic Data for $[M–N_4]^z$ Species

| Compound[a] | Couple | $E_{1/2}$,[f] v | $I$[b] | $i_d/C$,[d] µamp/m$M$ | Slope,[e] mv | Solvent |
|---|---|---|---|---|---|---|
| $Ni[C_6H_4(NH)_2]_2^0$ | ? | +0.23 | ... | −15.4 | 82 | DMSO |
| | $0 \rightleftharpoons -1$ | −0.88 | 1.1 | 7.7 | 63 | |
| | $-1 \rightleftharpoons -2$ | −1.59 | 1.0 | 7.5 | 61 | |
| | $+2 \rightleftharpoons +1$ | +0.73 | | | *i* | Acetone |
| | $+1 \rightleftharpoons 0$ | +0.14 | *c* | *c* | 59 | |
| | $0 \rightleftharpoons -1$ | −0.89 | | | 60 | |
| | $-1 \rightleftharpoons -2$ | −1.43 | | | 63 | |
| $Ni[4\text{-}i\text{-}PrC_6H_4(NH)_2]_2^0$ | $+2 \rightleftharpoons +1$ | +0.81 | ... | −24 | 87 | Acetone |
| | $+1 \rightleftharpoons 0$ | +0.09 | −2.7 | −31 | 53 | |
| | $0 \rightleftharpoons -1$ | −0.98 | 3.0 | 32 | 66 | |
| | $-1 \rightleftharpoons -2$ | −1.51 | 2.6 | 30 | 67 | |
| | $+2 \rightleftharpoons +1$ | +1.32 | ... | −20 | ... | $CH_2Cl_2$ |
| | $+1 \rightleftharpoons 0$ | +0.44 | ... | −25 | ... | |
| | $0 \rightleftharpoons -1$ | −0.77 | ... | 28 | ... | |
| | $-1 \rightleftharpoons -2$ | −1.4[i] | ... | 26 | ... | |
| $Pd[C_6H_4(NH)_2]_2^0$ | $+2 \rightleftharpoons +1$ | +0.78 | ... | −5.6 | 56 | DMSO |
| | $+1 \rightleftharpoons 0$ | +0.10 | ... | −7.2 | 65 | |
| | $0 \rightleftharpoons -1$ | −0.89 | 1.1 | 7.5 | 67 | |
| | $-1 \rightleftharpoons -2$ | −1.44 | 1.0 | 6.7 | 67 | |
| $Pt[C_6H_4(NH)_2]_2^0$ | $+2 \rightleftharpoons +1$ | +0.78 | ... | −5.3 | 53 | DMSO |
| | $+1 \rightleftharpoons 0$[h] | +0.23 | ... | −6.7 | 59 | |
| | $0 \rightleftharpoons -1$ | −1.01 | 1.0 | 6.6 | 65 | |
| | $-1 \rightleftharpoons -2$ | −1.70 | 0.92 | 6.2 | 67 | |
| $Co[C_6H_4(NH)_2]_2^0$ | ? | +0.61 | ... | −9.9 | 134 | DMSO |
| | $+1 \rightleftharpoons 0$ | −0.17 | 0.84 | −7.3 | 58 | |
| | $0 \rightleftharpoons -1$ | −0.80 | 1.0 | 8.1 | 71 | |
| | $-1 \rightleftharpoons -2$ | −1.83 | 0.92 | 6.4 | 61 | |
| $Ni[(CH_3CNC_6H_5)_2]_2I_2$ | $+2 \rightleftharpoons 0$ | −0.61 | 4.1 | ... | 35 | $CH_3CN$ |
| | $0 \rightleftharpoons -1$ | −1.60 | 2.1 | ... | 56 | |
| | $-1 \rightleftharpoons -2$ | −1.80 | 2.1 | ... | 56 | |
| $(Et_4N)[Ni(CH_3C_6H_3S_2)_2]$[g] | $-1 \rightleftharpoons -2$ | −0.52 | 0.97 | 7.2 | 56 | DMSO |
| | $-1 \rightleftharpoons -2$ | −0.58 | 2.8 | ... | 60 | $CH_3CN$ |
| | $-1 \rightleftharpoons -2$ | −0.40 | ... | 24 | ... | $CH_2Cl_2$ |

[a] Solution of the indicated compound used in measurements. [b] $i_d/m^{2/3}t^{1/6}C$ where $i_d$ is in µamp, $m$ in mg/sec, $t$ in sec, and $C$ in mmoles/l.; if there is an entry in this column the corresponding $E_{1/2}$ and slope values were determined at a dme; all waves less positive than ∼+0.1 v were measured at both a dme and a Pt electrode and good agreement (±10 mv) of $E_{1/2}$ values was obtained; waves obtained using a dme in general more closely approached reversible behavior, and $E_{1/2}$ and slope values using this electrode are given in columns 3 and 6. [c] Saturated solution, ratio of diffusion currents 0.9:1.1:1.0:1.0 as potentials decrease. [d] Data obtained on rotating Pt electrode. [e] Slope of plot of log $i(i_d - i)^{-1}$ *vs.* $E$, which for a reversible reaction at 25° is $58/n$ mv. [f] Potentials in DMSO, acetone, and acetonitrile solutions were measured *vs.* a saturated calomel electrode using KCl–agar salt bridge and 0.05 $M$ $(n\text{-}C_3H_7)_4NClO_4$ as the supporting electrolyte; measurements in dichloromethane were made as described[2] using 0.1 $M$ $(n\text{-}C_4H_9)_4NPF_6$ as the supporting electrolyte. [g] Data for established one-electron reaction[5] included for purposes of comparison. [h] See text, ref 24. [i] Poorly defined wave.

yields a broad wave due to the oxidation of iodide and $[M–N_4]^+$ at nearly the same potential. Cyclic voltammetry studies have further demonstrated the reversibility of the processes $+2 \rightleftharpoons +1$, $+1 \rightleftharpoons 0$, and $0 \rightleftharpoons -1$ for $Pd[(NH)_2C_6H_4]_2^0$. At a platinum electrode in DMSO equal anodic and cathodic peak currents were observed for each process.

Polarography of $Ni[C_6H_4(NH)_2]_2^0$ and of its 4-isopropyl derivative in acetone and dichloromethane shows four one-electron waves. In DMSO two reductive waves are seen in conjunction with a single (apparent) two-electron oxidation. The solvent dependence of the electrode reactions appears to be related to the stability of the nickel cations (*vide infra*).

Polarography of $Co[C_6H_4(NH)_2]_2^0$ in DMSO provides evidence for an incomplete electron transfer series. Oxidation to $[Co–N_4]^+$ and reduction to $[Co–N_4]^-$ and $[Co–N_4]^{-2}$ are observed. The number of electrons transferred in the oxidation at +0.61 v cannot be ascertained from diffusion current analysis. Unambiguous evidence for $[Co–N_4]^{+2}$ is, therefore, lacking. The monoiodide salt is reducible to the $z = 0, -1, -2$ members at potentials within ±20 mv of those in Table III. Hence, the authenticity of the first four members **4**–**7** of the series is assured.

Polarographic reduction of $Ni[(CH_3CNC_6H_5)_2]_2^{+2}$ as either the dinitrate or diiodide salt reveals in acetonitrile a two-electron reduction to the neutral member **14**, followed by two one-electron reductions to the $z = -1, -2$ species. The very negative half-wave potential implies[21] that the neutral complex should be very air unstable. This is indeed the case and solutions free from oxidation products could not be prepared, thereby precluding polarographic study of this complex. Nonetheless, the existence of the $z = +2, 0, -1, -2$ members of this series is believed to be established.

The body of polarographic data firmly establishes that the five neutral complexes are the central members **6** of their respective electron transfer series, and demonstrates that the nickel, palladium, and platinum series having the members $M[C_6H_4(NH)_2]_2^z$ are, by definition, complete. Efforts directed toward isolation and/or further identification of the species produced electrochemically are next considered. Each group of complexes, $[M–N_4]^z$, defined by its total charge $z$ is con-

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behavior is unclear. Despite the reasonable value of the slope (53 mv) for the $0 \rightleftharpoons +1$ couple given in Table III, this couple may not be truly reversible. However, epr results (*vide infra* and Table IV) demonstrate that the chemical and electrochemical oxidation products of $[Pt–N_4]^0$ are the same species.

Table IV. Epr Results for $[M–N_4]^z$ Complexes

| Complex | Medium | Solution $\langle g \rangle$ | Glass $g_1$ | Glass $g_2$ | Glass $g_3$ |
|---|---|---|---|---|---|
| $Ni[C_6H_4(NH)_2]_2^-$ | DMF–acetone[a] | 2.031[c] | 1.990 | 2.006 | 2.102 |
| $Pd[C_6H_4(NH)_2]_2^-$ | DMF–acetone[a] | 2.006 | 1.946 | 2.008 | 2.062 |
| $Pt[C_6H_4(NH)_2]_2^-$[b] | DMF–acetone[a] | 1.988 | 1.759 | 1.979 | 2.217 |

| Complex | Medium | Solution $\langle g \rangle$ $I^-$ salt | Solution $\langle g \rangle$ cpe[d] | Solid $g$ |
|---|---|---|---|---|
| $Ni[C_6H_4(NH)_2]_2^+$ | DMSO | 1.997[e] | . . . | 2.000[h] |
| $Pd[C_6H_4(NH)_2]_2^+$ | DMSO | 1.996 | 1.997 | 2.000[h] |
|  | DMF | 1.996 | . . . |  |
| $Pt[C_6H_4(NH)_2]_2^+$ | DMSO | 1.982 | 1.982 | 1.985[f] |
| $Co[C_6H_4(NH)_2]_2^0$ | DMF | 2.24[g] | . . . | . . . |

[a] 3:1, v/v. [b] Anisotropic hyperfine splitting for $^{195}Pt$ in glass: $|a_1| = 145$, $|a_2| = 200$, $|a_3| = 68$ gauss. [c] 2.034 observed in DMSO (ref 6). [d] Controlled potential electrolysis. [e] Complex unstable in DMSO, measurements made rapidly on fresh solutions. [f] Calculated mean value from $g_{\parallel} = 1.940$, $g_{\perp} = 2.009$. [g] Peak-to-peak width ~260 gauss; uncertainty ± 0.02 due to broad line. [h] Single absorption, no observable anisotropy.

sidered in turn except for that with $z = 0$, whose isolation and properties are detailed above.

**$[M–N_4]^{-2}$ Complexes.** Because of the extremely negative $E_{1/2}$ values for the $-1 \rightleftharpoons -2$ process, no chemical isolation of these dianions was attempted. The most comvincing evidence for their existence is the two-step two-electron reduction consistently observed for the neutral complexes. No further reduction was observed in any case, in accord with the formulation of the most reduced species as the terminal member **4** of the electron transfer series.

**$[M–N_4]^-$ Complexes.** Again, no chemical isolation was attempted because the negative potentials of the $-1 \rightleftharpoons 0$ process indicate extreme sensitivity of the monoanions to oxidation. However, epr results have provided extremely strong evidence that the initial reduction product of $[M–N_4]^0$, M = Ni, Pd, and Pt, is in fact the monoanion **5**. Controlled potential electrolysis at potentials slightly more negative than the $E_{1/2}$ value of the first reduction step of the neutral complexes yields species whose epr spectra in a glass reveal three principal $g$ values. The spectrum of the platinum reduction is reproduced in Figure 3, and $g$ values are given in Table IV. These data are compatible only with a metal-containing species with $S = 1/2$ for the following reasons. First, the monoanions $[MS_4C_4R_4]^-$, R = CN,[25] $CF_3$,[21] M = Ni, Pd, Pt, and $[M(S_2C_6H_3CH_3)_2]^-$, M = Ni, Pt[5] exhibit $g$-tensor anisotropies of magnitudes close to those observed here and the order of $(g_3–g_1)$, Pt > Ni > Pd, is partially preserved (Pt > Ni ~ Pd). All of these $[M–S_4]^-$ species have been isolated and can be converted chemically or electrochemically to the $z = -2$ and, in some cases, to the $z = 0$ species. Second, the observed $g$ value anisotropy is far too great for an organic free radical species, even if the electron is localized mainly on nitrogen. For example, in the iminoxy radical, $CH_3C{=}(NOH)C{=}(\dot{N}O)CH_3$, where the unpaired spin is localized largely on one nitrogen, the principal $g$ values are 2.0026, 2.0063, and 2.0095.[26] Third, the spectrum of the initial reduction product of $[Pt–N_4]^0$ (Figure 3) clearly reveals the hyperfine splitting from $^{195}Pt$ (33.7%, $I = 1/2$). All of the results point toward a marked analogy between $[M–S_4]^-$ species and these reduction products, which are, therefore, considered to be the $[M–N_4]^-$ member **5** of the electron transfer series. Although there is no direct evidence available bearing on the nature of the initial reduction product of $[Co–N_4]^0$, it appears reasonable to formulate it as $[Co–N_4]^-$.

**$[M–N_4]^+$ Complexes.** Each neutral complex may be oxidized by 1 equiv of iodine to the salt $M[C_6H_4(NH)_2]_2I$, which is a 1:1 electrolyte in fresh DMSO solution and which has magnetic properties consistent with one-electron oxidation of $[M–N_4]^0$. The cobalt salt is diamagnetic but solutions of the nickel, palladium, and platinum salts yield epr signals, as expected for $S = 1/2$ species. The observation of $g$ values near the free-electron value (2.0023) may indicate an essentially ligand based character of the odd electron, although it is noted that $g$ tensor anisotropy is resolvable in the powder of the platinum salt. No hyperfine structure was observed in solutions of the cations.

All available evidence strongly supports the similarity of the electrochemically generated and chemically prepared cations. The cobalt, palladium, and platinum salts are reversibly reduced polarographically to the $z = 0, -1, -2$ members.[27] Controlled-potential electrolysis of $[Pd–N_4]^0$ and $[Pt–N_4]^0$ at potentials slightly more positive than the $E_{1/2}$ values of their $+1 \rightleftharpoons 0$ couples produces radicals having $g$ values within experimental error of those found in solutions of the iodide salts. Both of these values are in satisfactory agreement with the polycrystalline $g$ values. Finally, in every case the iodide salts can be chemically reduced to their neutral forms. Shaking fresh DMSO or DMF solutions with mercury generates the intense, characteristic colors of the $[M–N_4]^0$ complexes. The cations present in the iodide salts are, therefore, believed to be the authentic members **7** of their respective electron-transfer series.[28]

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(25) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963); A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *ibid.*, **86**, 4580 (1964).

(26) I. Miyagawa and W. Gordy, *J. Chem. Phys.*, 30, 1590 (1959); M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 283 (1963).

(27) Fresh DMSO solutions of the nickel salt also are reduced polarographically to the $z = 0, -1, -2$ members, but at potentials up to 100 mv more cathodic than the corresponding values obtained from a solution of the neutral complex. These potential differences may indicate a degree of irreversibility (see also ref 24), but the situation is unclear due to decomposition of the cation in DMSO. Aged solutions (2–3 hr) of the salt in this solvent show no well-defined oxidation–reduction properties. Polarographic oxidation of the neutral complex proceeds in an apparent two-electron step, rather than two one-electron steps as observed for $[Pd–N_4]^0$ and $[Pt–N_4]^0$. The epr signal of the dissolved iodide salt in DMSO rapidly decays. These observations point toward a considerable instability of the nickel-containing cations in this strongly coordinating solvent.

(28) While we believe that the available evidence demonstrates the interrelationship of the cations of these iodide salts with other members of the electron-transfer series, thereby showing that the cations have the anticipated electrochemical behavior of the members 7, we do not claim a complete investigation or understanding of magnetic properties. Magnetic susceptibility measurements on palladium and platinum salts have not been possible because of the small amounts of material isolated. The moment of the nickel salt is too low for an isolated $S = 1/2$ complex but may be due to spin-exchange effects in the solid. Extremely low solubilities of all the iodide salts ($\lesssim 10^{-3}$ *M* in DMSO and DMF) have precluded susceptibility measurements of solutions and investigation of $g$-tensor anisotropies in glasses. Epr signals obtained from solutions of the paramagnetic salts appear to be of somewhat lower intensity than expected on the basis of solute concentration. The existence in solution of species in addition to (but, presumably, not instead of) simple $S = 1/2$ cationic complexes cannot, strictly speaking, be ruled out. However, the analytical results on the compounds formulated as $M[C_6H_4(NH)_2]_2I$, their method of preparation and polarographic behavior (*cf.* Table III), and the firmly established existence of $Ni[(CH_3CNC_6H_5)_2]_2^0$ (14) and $Ni[(CH_3CNC_6H_5)_2]_2^{+2}$ lend powerful support to the formulation of the one-electron oxidation products of the neutral complexes as $M[C_6H_4(NH)_2]_2^+$.

**$[M\text{–}N_4]^{+2}$ Complexes.** The polarographic results show that in DMSO two-step oxidations of $[Pd\text{–}N_4]^0$ and $[Pt\text{–}N_4]^0$ occur, strongly indicating the existence of the corresponding dications. The identification of the two-electron oxidation product of $[Ni\text{–}N_4]^0$ in DMSO is uncertain[29] in view of the instability of the monocation in this solvent,[27] but in acetone and chloroform $Ni[4\text{-}i\text{-}PrC_6H_3(NH)_2]_2^{+2}$ appears to be formed. Attempts were made to isolate salts of the cation **8** by halogen oxidation of $[M\text{–}N_4]^0$, M = Ni and Pt. Polarography in DMSO of the oxidation product of $[Pt\text{–}N_4]^0$ with 2 equiv of bromine indicates that a polybromide was probably formed. Waves corresponding to the +1 → 0 and 0 → −1 reductions were observed; however, the current in the range of the +2 → +1 reduction is anodic and probably results from the oxidation of polybromide. The reaction products of $[Ni\text{–}N_4]^0$ with 2 equiv of either bromine or iodine show no well-defined reduction waves in DMSO. The iodine reaction product has been partially characterized; it analyzes satisfactorily for $NiC_{12}H_{12}N_4I_2$, and is diamagnetic. A similar product has been obtained from the reaction of 2 equiv of iodine with $Ni[4\text{-}i\text{-}PrC_6H_3(NH)_2]_2$. This material is sufficiently soluble in dichloromethane for measurement; it shows reductions to the $z = 0$ and $-1$ species and a definite, though poorly developed, wave due to reduction to $z = -2$. No reduction from +2 to +1 is observed. Rather, a wave due to iodide oxidation occurs at potentials more cathodic than the potential for the $+2 \rightleftharpoons +1$ reaction observed in a dichloromethane solution of $Ni[4\text{-}i\text{-}PrC_6H_3(NH)_2]_2^0$. Iodine reduces to triiodide in acetone at +0.60 v.[30] Comparison with the potentials in Table III reveals that iodine is not a sufficiently strong oxidizing agent to effect the $[Ni\text{–}N_4]^0 \rightarrow [Ni\text{–}N_4]^{+2}$ oxidation in acetone and, presumably, also in tetrahydrofuran in which the diiodide product was prepared. A likely formulation of both nickel-containing oxidation products is $[Ni\text{–}N_4]I_3 \cdot [Ni\text{–}N_4]I$.

**Qualitative Consideration of Donor Atom Effects on Electron Transfer Behavior.** A particularly advantageous feature of complexes of structural type **3** is that the donor atom set $X_2Y_2$ can be varied without disturbing the remainder of the ligand structure. We have previously shown that the nature of X and Y exert a profound effect on half-wave potentials of a given couple for the same metal.[4] For purposes of comparison potentials of interest for four series are collected in Table V. The comparison is justified because of the close similarity of geometrical[31] and electronic[35] structures for complexes of a given charge type.

**Table V.** Comparison of Half-Wave Potentials for $[Ni\text{–}X_2Y_2]^z$ Complexes (**3**)

| | $E_{1/2}{}^a$ | |
|---|---|---|
| $[Ni\text{–}X_2Y_2]$ | $-2 \rightleftharpoons -1$ | $-1 \rightleftharpoons 0$ |
| $[Ni\text{–}N_4]$ | $-1.59^b$ | $-0.88^b$ |
| $[Ni\text{–}N_2S_2]$ | $-1.04^b$ | $-0.19$ |
| $[Ni\text{–}S_4]$ | $-0.51$ | $+0.45$ |
| $[Ni\text{–}O_2S_2]$ | $-0.43$ | $+0.38$ |

[a] All data obtained in DMSO solution (0.05 $M$ $(n\text{-}Pr)_4NClO_4$ supporting electrolyte) at a rotating platinum electrode unless otherwise stated; all potentials measured *vs.* saturated calomel electrode using KCl–agar salt bridge. [b] Measured at a dropping mercury electrode.

The potentials in Table V reveal that in all cases the $z = -2, -1$, and 0 members can be detected polarographically and that the orders of oxidative stability of mono- and dianions are about the same, *viz.*, $[Ni\text{–}N_4] < [Ni\text{–}N_2S_2] < [Ni\text{–}S_4] \lesssim [Ni\text{–}O_2S_2]$. $[Ni\text{–}O_4]$ anions cannot be definitely placed in this series because of the uncertainty concerning the electronic structure of the monoanion.[2] We have attempted to interpret this stability order by the performing of a rather extensive set of molecular orbital calculations using the extended Hückel method,[36] but the results have been inconclusive. No consistent correlations have been found between the experimental potentials and calculated energies of orbitals implicated in electron addition or removal, charges on ligands or on metals, or total electronic energy differences between adjacent members of a series. Thus, only a qualitative rationalization of the observed stability order can be offered at present.

Vlček[37] has advanced the interesting postulate that the potentials of the oxidation–reduction couples of complexes should behave with respect to substitution on the parent ligand as would those of the corresponding free ligand couples. If substitution may be liberalized so as to include variation in donor atom sets $X_2Y_2$ in **3**, it is believed that this postulate provides the simplest qualitative rationalization of observed stability orders. In applying it we assume that the complexes are undissociated, *i.e.*, that there are insufficient concentrations of 1:1 complexes, free ligands, and uncoordinated metal ions to have important effects on the order of half-wave potentials. Data required to apply this postulate most meaningfully are the potentials $E_{xy}{}^{21}$ and $E_{xy}{}^{10}$ which would be most appropriately compared with the potentials of the

$$[C_6H_4XY]^{-2} \underset{}{\overset{E_{xy}{}^{21}}{\rightleftharpoons}} [C_6H_4XY]^{-} \underset{}{\overset{E_{xy}{}^{10}}{\rightleftharpoons}} [C_6H_4XY]^0$$

$-2 \rightleftharpoons -1$ and $-1 \rightleftharpoons 0$ couples, respectively, of the complexes. Ligand potentials for the X = Y = O case are readily obtained by reducing *o*-benzoquinone and other *o*-quinones; for a number of $[M\text{–}O_4]^{-2}$ complexes (M = Cu, Ni) Vlček's postulate has been borne

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[29] Our previous assertion[4] that the two-electron wave at +0.19 v (corrected to +0.23 v in this work) observed in a DMSO solution of $Ni[C_6H_4(NH)_2]_2^0$ arises from the $0 \rightleftharpoons +2$ couple must now be viewed with caution.

[30] Tribromide and triiodide are implicated in the electrochemical oxidation of iodine and bromine in acetonitrile; *cf.* A. I. Popov and D. H. Geske, *J. Am. Chem. Soc.*, 80, 1340, 5346 (1958).

[31] Much supporting evidence is available which shows that nickel complexes of types **1** and **2** are planar when $z = -2, -1, 0$. X-Ray structural determinations of salts containing $[NiS_4C_4(CN)_4]^{-2}$,[32] $[NiS_4C_4(CN)_4]^{-}$,[33] and $[NiS_4C_4Ph_4]^0$[34] reveal these complexes to be planar. Because of a convincing similarity between electronic properties of type **1** complexes and those in Table V, for a given charge $z$, the latter complexes are assumed planar for $z = -2, -1, 0$.

[32] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965).

[33] C. J. Fritchie, Jr., *Acta Cryst.*, 20, 107 (1966).

[34] D. Sartain and M. R. Truter, *Chem. Commun.*, 382 (1966).

[35] All dianions and neutral complexes of this group which have been isolated are diamagnetic. All neutral complexes have characteristically rich electronic absorption spectra. The species $[Ni\text{–}N_4]^-$ (*cf.* Table IV) $[Ni\text{–}N_2S_2]^-$,[6] $[Ni\text{–}S_4]^-$,[5] and $[Ni\text{–}O_2S_2]^-$[4] possess doublet ground states and highly anisotropic $g$ tensors which may be considered characteristic of electronically similar monoanions.

[36] M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, **4**, 44 (1966). We thank Mr. M. Zerner for use of computer programs and assistance with the calculations. It is to be noted that calculations of this sort have been useful in rationalizing half-wave potentials of a number of metal porphyrin complexes (R. H. Felton and H. Linschitz, *J. Am. Chem. Soc.*, 88, 1113 (1966)).

[37] A. A. Vlček, *Z. Anorg. Allgem. Chem.*, **304**, 109 (1960); *Progr. Inorg. Chem.*, **5**, 211 (1963).

out by direct comparison of experimental potentials.[2] However, in the series of interest here ligand potential data are uniformly unavailable. The required quinonediimine is too unstable to permit measurement. Dithia-*o*-quinones and thia-*o*-benzoquinoneimine are unknown. The required potentials could also be obtained from oxidation of the anions $C_6H_4XY^{-2}$ but none of these has been definitely characterized. Thus, a quantitative comparison between ligand and complex potentials appears thwarted.

If comparison of potentials is broadened to include nickel complexes of types **1**, **3**, and **14**, some qualitative conclusions can be reached. Like $Ni[C_6H_4(NH)_2]_2^{-2}$, $Ni[(CH_3CNC_6H_5)_2]_2^{-2}$ is more easily oxidized than $Ni[C_6H_4O_2]_2^{-2}$,[2] both of which are much less oxidatively stable than $[NiS_4C_4(CN)_4]^{-2}$. This is just the order of oxidative stability of the ligands, *viz.*, $(CH_3CNC_6H_5)_2^{-2} < C_6H_4O_2^{-2}$ [2] $< (NC)_2C_2S_2^{-2}$ [38] as measured from half-wave potentials. (Biacetylbisanil undergoes a two-electron reduction at −1.82 v in acetonitrile *vs.* sce.) This observation, in addition to those already reported,[2] further supports Vlček's ideas and leads to the following general conclusion. Free ligands which are most stable in the anionic form tend to stabilize the $z = -2, -1$, and (possibly) 0 members of their electron transfer series whereas free ligands most stable in the neutral (oxidized) form tend to stabilize the $z = 0, +1$, and $+2$ members of their series. Thus, the complexes **2** are most stable as mono- and dianions; cationic complexes are relatively unstable due presumably to the instability of the 1,2-dithione structure. Similarly, anions in the [M–$N_4$] series can be detected but are extremely oxidatively unstable relative to the $z = 0, +1, +2$ members; the dianion of *o*-phenylenediamine is undoubtedly quite unstable in an oxidative sense with respect to the quinonediimine. Finally, the [M–$N_4$] system obviously benefits at the extremes of its electron transfer series from the generally effective coordinating ability of both imino and amido nitrogen donor atoms, which no doubt enhances the kinetic stability of the terminal and intermediate members.

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[38] H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, 84, 4756 (1962).

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# Optical Rotatory Dispersion Studies on the Borotartrate Complexes and Remarks on the Aqueous Chemistry of Boric Acid[1,2]

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**Abstract:** Through precise measurements of the optical rotatory dispersion of solutions of tartaric acid, and its mixtures with boric acid, at controlled pH, apparent Drude parameters for the borotartrate complex and concentrations of free tartrate in the mixtures have been derived. Computations of equilibrium constant indicate the dominant complex to be of 1:1 stoichiometry. The complex is considered to be a chelate of tetrahedrally coordinated B(III) which involves one tartrate hydroxyl and the nearer carboxyl group. The complex's strong acid character is derived through displacement of the hydroxyl proton by boron, as the latter changes its coordination to tetrahedral from the trigonal planar coordination of boric acid. A second stage of acid dissociation occurs above pH 4, and evidence is reported suggesting possible polyborotartrate complexes also.

That the optical rotation of tartaric acid is modified by addition of boric acid has been known since the early work of Biot in 1832.[3] The system has been studied frequently, and it has been generally agreed that some species of complex forms. The stoichiometry of the complex has been suggested variously to be two boric acids per tartrate,[4] one boric acid to one tartarate[5,6] and one boric acid to two tartrates.[7–11] Evidence presented for the last formulation—an apparent maximum in the rotation at a solution composition corresponding to one mole each of tartrate, bitartrate, and boric acid, and formation (though with difficulties) of a solid phase approximating this formulation—seemed for some time to be most compelling. Analogy to a boric acid–salicylic acid complex of similar stoichiometry[12,13] gave additional support.

After a gap of some 20-odd years, from reinvestiga-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

[3] *Cf.* T. M. Lowry, "Optical Rotatory Power," Longmans, Green and Co., London, 1935; reprinted by Dover Publishers, Inc., New York, N. Y., 1964.

[4] M. Amadori, *Gazz. Chim. Ital.*, **61**, 215 (1931).

[5] T. M. Lowry and P. C. Austin, *Phil. Trans. Roy. Soc. London*, **222A**, 249 (1922).

[6] S. G. Burgess and H. Hunter, *J. Chem. Soc.*, 2838 (1929).

[7] T. M. Lowry, *ibid.*, 2853 (1929).

[8] W. D. Bancroft and H. L. Davis, *J. Phys. Chem.*, **34**, 2479 (1930).

[9] B. Jones, *J. Chem. Soc.*, 951 (1933).

[10] I. Jones and F. G. Soper, *ibid.*, 1836 (1934).

[11] H. T. S. Britton and P. Jackson, *ibid.*, 1002 (1934).

[12] E. Johns (1878), cited in ref 13.

[13] A. Rosenheim and H. Vermehren, *Ber.*, **57**, 1337, 1828 (1924).