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Electron-Transfer Series of the $[M\text{-}N_4]$ Type. Complexes Derived from the Quadridentate Ligand 1,3-Di(2-aminophenylamino)propane.

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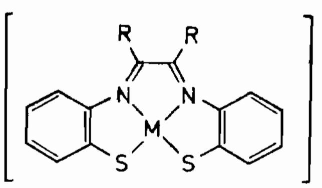
New electron-transfer series of the $[M-N_4]^z$ type which are derived from quadridentate ligands such as 1,3-di(2-aminophenylamino)propane, are described. Electrochemical studies on a palladium complex provide evidence for a 5-membered series with $z = -2, -1, 0, +1,$ and $+2$. Four members, with $z = -2, -1, 0,$ and $+1$ were detected for the comparable nickel complexes. In general the electronic properties of these quadridentate systems are very similar to their bis-bidentate analogues derived from o-*phenylenediamine.*

Introduction

Recent interest in metal complexes showing extensive electron-transfer series has been confined largely to planar bis-bidentate systems with ligands of the dithiolate type, and these compounds have been the subject of comprehensive reviews.[1,2]

Analogous systems in which the S donor atoms have been replaced by NH,[3,4,5,6] O,[3,7,8] and Se,[9,10] have also received some attention. Relatively fewer electron-transfer series involving quadridentate ligands have been described. The $[M-N_2S_2]$ system (I) has been known for some time,[5,11] and it has been shown[5] that the presence of the conjugated bridge between the two o-thioaniline units causes the reduction-oxidation behaviour to differ little from the analogous bis-bidentate system (II) (X = S, Y = NH). Reduction of (I) ($R = CH_3$, $z = 0$, M = Ni) with borohydride gives an anionic species (III) with a saturated bridge between the NS units.[12] Another type of $[M-N_2S_2]$ quadridentate system (IV), derived from diketone-bisthiosemicarbazides shows two well defined reduction steps but irreversible oxidation.[13] The only $[M-N_4]$ quadridentate system which has been described pre-



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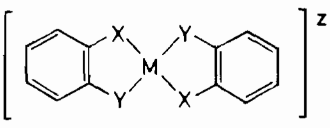

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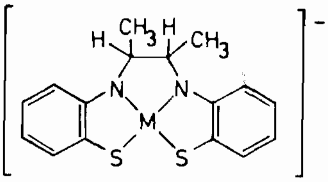

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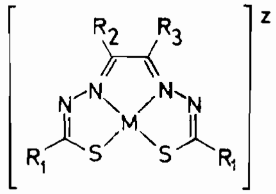

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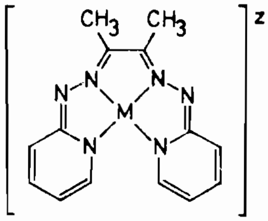
viously* is (V), for which all five members of the series with z = +2, +1, 0, −1, −2 have been detected polarographically when M = Pd.[14] This paper, the



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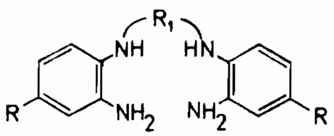
first in a series describing metal complexes of polydentate ligands containing the o-phenylenediamine unit, considers electron-transfer series of the [M—N$_4$] type which are derived from the quadridentate ligands (VI).



VI

Experimental Section

Analyses were performed by MichoTech Laboratories, Skokie, Illinois and the Spang Microanalytical Laboratory, Ann Arbor, Michigan. Electronic spectra were recorded on a Cary Model 14M spectrophotometer and infrared spectra as nujol and hexachlorobutadiene mulls on Beckmann IR10 and Perkin Elmer 457 spectrometers. Magnetic measurements were made on an Alfa magnetic balance using the Faraday method. Polarographic data were obtained by using a Heath Kit Model EUW-401 polarograph equipped with three electrode geometry.

The Ligands (VI). The syntheses of 1,2-di(2-aminophenylamino)ethane (VI, R$_1$ = $-(CH_2)_2-$, R = H) and 1,3-di(2-aminophenylamino)propane (VI, R$_1$ = $-(CH_2)_3-$, R = H) have been reported previously.[15] 1,3-Di(4-methyl-2-nitrophenylamino)propane was prepared by a similar method (yield 35%) as fine orange needles (mp 142-144°) after recrystallization from chloroform, and gave on reduction with hydrazine and 5% palladium-carbon 1,3-di(2-amino-4-methylphenylamino)propane (VI, R$_1$ = $-(CH_2)_3-$, R = CH_3) which was recrystallized from chloroform-hexane as fine white needles, mp 96.5-98° (yield 65%). Found C, 71.80; H, 8.58; N, 19.84; $C_{17}H_{24}N_4$ requires C, 71.79; H, 8.51; N, 19.70%.

1,3-Di(2-aminophenylamino)propanonickel) (*VII*). To a stirred solution of 1,3-di(2-aminophenylamino)-propane (1 g) in methanol (50 ml) was added a solution of nickel chloride hexahydrate (1.8 g) in water (5 ml) followed by a saturated solution of methanolic ammonia (10 ml). The resulting suspension was stirred in an open beaker for 24 hr, with further methanolic ammonia being added periodically to replace methanol lost by evaporation. The crude product was collected by filtration and washed with large quantities of aqueous ammonia, methanol and acetone. Soxhlet extraction into acetone gave 1,3-di(2-aminophenylamino)propanonickel as small needles with a purple sheen. Found C, 57.39; H, 5.05; N, 17.94; $C_{15}H_{16}N_4Ni$ requires C, 57.92; H, 5.19; N, 18.01%.

1,3Di(2-amino-4-methylphenylamino)propanonickel, (*VIII*) was prepared in a similar manner. Found C, 59.86; H, 6.04; N, 16.72; $C_{17}H_{20}N_4Ni$ requires C, 60.22; H, 5.95; N, 16.52%.

1,3-Di(2-aminophenylamino)propanopalladium, (*IX*). Concentrated aqueous ammonia (10 ml) and palladium(II) nitrate (1.1 g) in water (10 ml) were added to a solution of 1,3-di(2-aminophenylamino)propane (1 g) in methanol (200 ml). The resulting yellowish suspension was stirred in an open beaker for 10 hr, with methanolic ammonia being added periodically to replace solvent lost by evaporation. The product was collected by filtration and washed with water, methanol and chloroform until the washings were a pale blue colour. The resulting deep-blue very fine needles were dried under vacuum. Found C, 48.68; H, 4.16; N, 16.02; $C_{15}H_{16}N_4Pd$ requires C, 49.12; H, 4.40; N, 15.28%. Purification by Soxhlet extraction into acetone as for the nickel complexes (VII) and (VIII) was not successful for the palladium complex (IX), giving only a brown non-crystalline material.

Dithiocyanato[1,3-di(2-aminophenylamino)propane]-nickel(II). To a solution of $NiCl_2.6H_2O$ (300 mg) and 1,3-di(2-aminophenylamino)propane (250 mg) in deoxygenated methanol (25 ml) was added hydrated lithium thiocyanate dissolved in a small volume of methanol. The mixture was allowed to stand under nitrogen for 1 hr when pink-purple crystals of dithiocyanato[1 3-di(2-aminophenylamino)propane]nickel-(II) separated slowly. These were collected, washed with methanol and ether and dried under vacuum (Yield 388 mg 77%). Found C, 47.05; H, 4.72; N, 19.41: $C_{17}H_{20}N_6S_2Ni$ requires C, 47.35; H, 4.67; N, 19.49%. λ_{max} (nujol mull) 910 and 535 nm.

1,3-Di(2-aminophenylamino)propanonickel iodide, [$NiC_{15}H_{16}N_4$]*I*. A solution of iodine (120 mg, 0.47 mmole) in tetrahydrofuran (10 ml) was added in portions to a stirred suspension of (VII) (290 mg 0.94 mmole) in acetone (10 ml). The mixture was stirred vigorously under nitrogen for 12 hr and the product collected, washed with acetone, methanol and ether, and dried in vacuum. (Yield 345 mg 84%). Found C, 40.97; H, 3.70; N, 13.11; $C_{15}H_{16}N_4NiI$ requires C, 41.14; H, 3.68; N, 12.79%.

Nickel and palladium complexes of 1,2-di-(2-aminophenylamino)ethane (VI, R$_1$ = $-(CH_2)_2-$, R = H)

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* Quadridentate ligands derived from salicylaldehyde and o-aminobenzaldehyde which give nickel and cobalt complexes having charges delocalized through six-membered chelate rings often show well defined polarographic oxidation and reduction waves (G. Costa, A. Puzeddu and L.B. Stefani, *Inorg. Nucl. Chem. Letters*, *6*, 191 (1970), B.M. Higson and E.D. McKenzie, *Inorg. Nucl. Chem. Letters*, *6*, 209 (1970), R. Bratchley, M. Green and P.A. Tasker, unpublished results).

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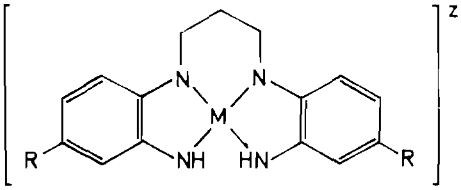
could not be obtained using the conditions which were successful for (VII), (VIII) and (IX).



[VII] M=Ni, R=H
[VIII] M=Ni, R=CH_3
[IX] M=Pd, R=H

Results and Discussion

When the quadridentate ligands ([VI] R_1 = $-(CH_2)_3-$) were treated in air with basic solutions containing nickel(II) or palladium(II) salts, very insoluble blue materials separated slowly. These highly coloured products may be formulated as the neutral species (VII), (VIII) and (IX) with z = 0, in which the ligand has formally lost 2 protons and 2 hydrogen atoms on complexation with the divalent metal ion. The structures (VII, (VIII) and (IX) are supported by the following pieces of evidence:

(1) Chemical analyses are compatible with (VII), (VIII) and (IX) and do not allow the presence of counterions in the molecular formulae.

(2) In the mass spectrum of (VII) the ion of highest m/e coresponds to a parent ion $C_{15}H_{16}N_4Ni^+$. Tihs is the molecular formula of (VII) which has four less hydrogen atoms than that of the uncomplexed ligand ($C_{15}H_{20}N_4$). The relative intensities of peaks in the parent ion region give reasonable agreement with the natural abundances of the isotopes of nickel.

(3) Examination of i.r. spectra in the region 3000-4000 cm^{-1} provides further evidence for the loss of amine hydrogen atoms from the ligand molecules during the reactions to give the complexes (VII), (VIII) and (IX). 1,3-Di(2-aminophenylamino)propane (VI) (R_1 = $-(CH_2)_3-$ R = H) shows a complex pattern of NH-stretching bands in this region (spectrum A, Figure 1), whereas the nickel complex (VII) has just a single band (spectrum B). Such striking simplification in the NH stretching region is not observed on complexation to give the conventional octahedral complex dithiocyanato[1,3-di(2-aminophenylamino)propane]nickel(II) (spectrum C). In this complex the ligand formula remains unchanged ($C_{15}H_{20}N_4Ni(SCN)_2$), and the electronic spectrum closely resembles other octahedral dithiocyanatotetraminenickel(II) complexes.[16,17]

(4) At room temperature in the solid state (VII), (VIII), and (IX) are diamagnetic. This is to be expected for a low-spin planar arrangement of the $M-N_4$ nit when it is associated with an even number of electrons, e.g. when z = 0.

(5) In general the properties of the neutral complexes (VIII), (VIII), and (IX) are remarkably similar to the analogous bis-bidentate systems derived from *o*-phenylenediamine (*vide infra*). Careful chemical studies[4] have shown that the latter are best represented by structures analogous to (VII), (VIII), and (IX), *i.e.* by (II) with X = Y = NH and z = 0. An X-ray structure determination[18] of bis(*o*-phenylenediamino)nickel has confirmed the planarity of the molecule. Additionally, the bond lengths in the chelate rings have provided further evidence for extensive π-delocalization.

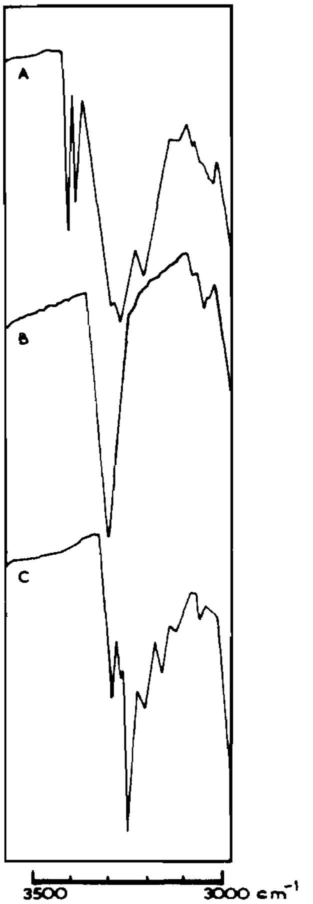


Figure 1. Infrared spectra (nujol mulls, 3000-3500 cm^{-1}) of 1,3-di(2-aminophenylamino)propane (A), 1,3-di(2-aminophenylamino)propanonickel (B) and dithiocyanato[1,3-di(2-aminophenylamino)propane]nickel(II) (C).

The principal absorption bands in the electronic spectra of the spectra of the complexes (VII), (VIII), and (IX) are given in Table I. For the nickel complexes the dominant feature in each spectrum is the very strong band observed around 800 nm. Bis(*o*-phenylenediamino)nickel (II) (X = Y = NH, M = Ni, z = 0) shows a related intense absorption at 790 nm, but only in the solid state are lower energy shoulders at 865 and 915 nm observed. Similar lower energy shoulders are detectable in solution for the complexes (VII) and (VIII).

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Table I. Electronic spectra (300-11,00 nm), recorded as dimethyl sulphoxide solutions.

Complex	λ_{max} in nm. Molar extinction coefficients in parentheses									
[VII], z=0	940sh[a] (8280)	807 (83,500)	680sh (10,000)		530sh (2440)	465 (2010)	423 (2660)		320sh (7800)	308
[VIII], z=0	940 (9200)	825 (63,000)	680 (5220)	635sh (4220)	535sh (1450)	473 (1080)	428 (1580)	412sh (1450)	350sh (4050)	(12,000)
$\{Ni[C_6H_4(NH)_2]_2\}^0$ [b] [II], X=Y=NH		790 (54,900)	650 (5640)	560sh (2140)	520 (1560)		420sh (1260)	400 (1160)	335 (4210)	310sh
[IX], z=0	825 (26,600)	794 (26,200)	631 (3790)	571 (3610)	525 (3520)	452 (3170)	429sh (2850)	345 (4040)	323 (4240)	
$\{Pd[C_6H_4(NH)_2]_2\}^0$ [b] [II], X=Y=NH		780 (48,200)	621 (1700)	568 (1280)	511 (1130)	458 (924)		350 (3870)	311 (5520)	(4670)

[a] sh = shoulder [b] A.L. Balch and R.H. Holm, *J. Amer. Chem. Soc.*, *88*, 5201 (1966).

Table II. Electrochemical data

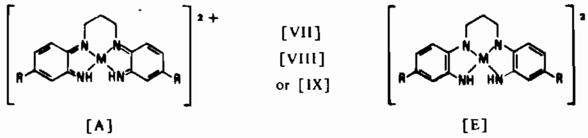
Compound/Solvent	z=−1 $E_{1/2}$ [a]	→ z=−2 $E_{3/4}-E_{1/4}$ [b]	z=0 $E_{1/2}$	→ z=−1 $E_{3/4}-E_{1/4}$	z=0 $E_{1/2}$	→ z=+1 $E_{3/4}-E_{1/4}$	z=+1 $E_{1/2}$	→ z=+2 [c] $E_{3/4}-E_{1/4}$
[VII]/DMSO	−1.61	62	−0.89	62	+0.14	51	*f*	
/acetone	−1.65	62	−1.01	55	+0.11	53	+0.56 [d]	
[VIII]/DMSO	−1.65	56	−0.93	62	+0.04	64	*f*	
$\{Ni[C_6H_4(NH)_2]_2\}$								
/DMSO [e]	−1.59		−0.88		+0.23			
/acetone [e]	−1.43		−0.89		+0.14		+0.73	
[IX]DMSO	−1.44	62	−0.87	55	+0.07	51	+0.59	70
$\{Pd[C_6H_4(NH)_2]_2\}^z$								
/DMSO [e]	−1.44		−0.89		+0.10		+0.78	

[a] Half wave potential (volts) measured *vs* SCE with $[(C_2H_5)_4N][ClO_4]$ (0.05 *M*) as the supporting electrolyte, using a DME. [b] $E_{3/4}-E_{1/4}$ in mV. For a reversible one-electron wave $E_{3/4}-E_{1/4}$ = 56 mV. [c] This process measured at a rotating platinum electrode (600 rpm). [d] Poorly defined wave. [e] A.L. Balch and R.H. Holm, *J. Amer. Chem. Soc.*, *88*, 5201 (1966). [f] Wave obscured by electrode coating.

The spectra of the palladium complex (IX) and bis-(*o*-phenylenediamino)palladium (II) (X = Y = NH, M = Pd z = 0) are remarkably similar in most of the visible region, the main difference being the occurrence of two closely spaced intense absorptions at 825 and 794 nm in the quadridentate systems (IX), which are possibly overlapping in the bis-bidentate analogue, giving only a single band at 780 nm.[4]

Similarities in electronic properties of the quadridentate and bis-bidentate systems are further emphasized by an examination of half-wave potentials required for reduction and oxidation. These data are summarized in Table II. The palladium complex (IX) shows two one-electron reduction processes and two one-electron oxidation processes, corresponding to interconversion of all five members A, B, C, D and E in the electron-transfer series shown in Figure 2. The stable limits of this series are defined formally by metal(II) complexes of oxidized or reduced forms of the ligand as in (A) and (E). The half-wave potentials for (IX) are very similar to those of the bis(*o*-phenylenediamino)palladium system.

Interconversion of members of the series shown in Figure 2 is also observed for the nickel complexes (VII) and (VIII) except that a polarographic wave corresponding to the process (A)⇌(B) could not be detected clearly. At the potentials expected for the oxidation of the nickel species (B) a rotating platinum electrode was rapidilly coated with a black deposit, and it appears that the monocations (B) derived from (VII) are not stable in solution. It has been reported[4] that cationic species derived from bis(*o*-phenylnediamino)nickel also have a limited stability in solution. Cyclic voltammetry studies on an acetone solution (VIII) established that the processes 0 ⇋ −1, −1 ⇋ −2 and 0 ⇋ +1 are reversible.



$$[MC_{15}H_{14}N_4R_2]^{2+} \rightleftharpoons [MC_{15}H_{14}N_4R_2]^{+} \rightleftharpoons [MC_{15}H_{14}N_4R_2]^{0} \rightleftharpoons [MC_{15}H_{14}N_4R_2]^{-} \rightleftharpoons [MC_{15}H_{14}N_4R_2]^{2-}$$

[A] [B] [C] [D] [E]

Figure 2. The Five-Membered Electron-Transfer Series Derived from the Complexes [VII], [VIII] and [IX].

On oxidation with iodine the neutral complexes [C] were converted to the monocations [B] which were isolated as their highly insoluble iodide salts. When [C] is treated with more than one equivalent of iodine the insoluble product was shown by chemical analysis to have incorporated further iodine. It is not clear whether this material contains the dication[A] or the monocation [B] which has separated as a mixture of the triiodide[4] salt $[MC_{15}H_{14}N_4R_2]I_3$ and the iodide salt $[MC_{15}H_{14}N_4R_2]I$.

A general comparison of the quadridentate systems (VII), (VIII) and (IX) with their bis-bidentate analogues reveals that the 1,3-propane bridge between the two *o*-phenylenediamine units causes remarkably little difference in electronic properties. In this respect the choice of the propane bridge is probably fortuitous since it allows the four nitrogen donors to achieve a similar coordination geometry to that in the bis(*o*-phenylenediamino)metal complexes. It has been established [19,20] that a non-branching quadridentate ligand with alternating chelate rings containing 5, 6, and 5 members allows a planar arrangement of the donor atoms. It is, therefore, significant that the quadridentate ligand (VI) (R_1 = $-(CH_2)_2-$, R = H), with an ethane bridge between the *o*-phenylenediamine units, gives no neutral complexes of the type (VII) or (IX) when used under the same synthetic conditions.

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