caution and evaporated slowly at room temperature in an open hood (cf. ref 43).

Caution! Perchlorates are not only potentially explosive in the writing of safety notes but also actually explosive in the laboratory. We are sad to say that at the same time we were drawing up this paper, a chemist was killed on the campus at Orsay, due to an explosion of lithium perchlorate handled in tenths of grams in methanolic concentrated solutions within a metallic glovebox.

When noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates.

Acknowledgment. This work was partially supported by the "Programa de Acciones Integradas Hispano-Francesas" and the Comisiõn Asesora de Investigaciõn Cientĩfica y Tẽcnica (Proyecto PB85-0190). We are grateful to Professor O. Kahn for helpful discussions and to Dr. J. P. Renard (IEF at Orsay) for making available the mutual inductance bridge.

Registry No. 1, 110015-67-3; 2, 110015-69-5; 3, 110015-71-9.

Supplementary Material Available: Listings of atomic coordinates, thermal parameters, weighted least-squares planes, and bond distances and angles for both compounds **1** and **3** (67 pages); listings of structure factor amplitudes (63 pages). Ordering information is given on any current masthead page.

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[43] *J. Chem. Educ.* **1985**, *62*, 1001. *Chem. Eng. News* **1983**, *61* (Dec 5), 4; **1963**, *41* (July 8), 47. Please note that the reference in the notice to authors (*Inorg. Chem.* **1987**, *26*(1), 4A-6A) must read: *J. Chem. Educ.* **1973**, *50*, A335.

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Dipartimento di Chimica, Università di Firenze, 50144 Florence, Italy, and ISSECC, 50132 Florence, Italy

Dinickel and Dicopper Complexes with N,N-Linked Bis(cyclam) Ligands. An Ideal System for the Investigation of Electrostatic Effects on the Redox Behavior of Pairs of Metal Ions

Mario Ciampolini,*[1a] Luigi Fabbrizzi,*[1b] Angelo Perotti,[1b] Antonio Poggi,[1b] Barbara Seghi,[1b] and Fabrizio Zanobini[1c]

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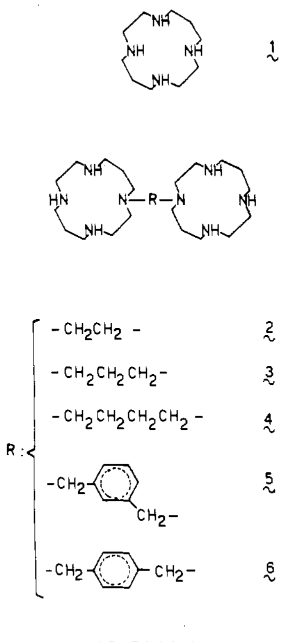
A novel family of bis(macrocycles) in which two cyclam subunits are linked through nitrogen atoms by a carbon chain R of varying length (R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, *m*-xylyl, *p*-xylyl) has been designed. Synthesis is based on the condensation of the readily available intermediate *N,N′,N″*-tritosylcyclam (2 equiv) with an X–R–X fragment (X = Br or OTs). Electrochemical investigation has shown that the corresponding dinickel(II) and dicopper(II) bis(macrocyclic) complexes undergo a two-electron-oxidation process, according to two reversible one-electron steps, whose redox potentials are separated by the quantity $\Delta E°$. The value of ΔE is related to the comproportionation (or *valence scrambling*) equilibrium $[M^{III}M^{III}(L)]^{6+} + [M^{II}M^{II}(L)]^{4+} \rightleftharpoons 2[M^{III}M^{II}(L)]^{5+}$ and results from the combination of a statistical fixed contribution and a term that reflects the electrostatic repulsion between the metal centers of the dinuclear complex. It has been found that the electrostatic repulsion term decreases when the distance between the metal centers is increased, according to a hyperbolic mode, but does not show any definite dependence upon the macroscopic values of the dielectric constant of the explored media. Moreover, the electrostatic term significantly varies with the stereochemical features of each metal center in its oxidation state (II or III), which cannot be any longer considered as simple point charges.

Introduction

The preparation and properties of a large number of homodimetallic complexes have been described over the past two decades. Some of these dinuclear species display redox activity in solution disclosing two consecutive one-electron-redox steps. The separation of the potentials associated with each redox event, ΔE, may range from 36 mV (limiting case in which the two equivalent redox centers behave independently), to some hundreds of millivolts for complexes in which strong mutual interactions exist between metal centers. The communication between the two metals may occur through two main paths: (i) electronic (direct interaction or delocalization through a bridging coordinating unit) and/or (ii) electrostatic. The separation of the two contributions may not be straightforward.[2]

Recently a novel class of ligands capable of binding pairs of metal ions quite strongly has been introduced: the bis(macrocycles). In these ligating systems two cyclic polyaza subunits are linked together either through an aliphatic chain joining two nitrogen atoms (N,N′-bis(macrocycles))[3-7] or by a covalent bond joining two carbon atoms (C,C′-bis(macrocycles)).[8-12] Each subunit may incorporate a transition-metal ion to give a very stable

Chart I



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[1] (a) Università di Firenze. (b) Università di Pavia. (c) ISSECC.

[2] Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1 and references therein.

[3] Ciampolini, M.; Micheloni, M.; Nardi, N.; Vizza, F.; Buttafava, A.; Fabbrizzi, L.; Perotti, A. *J. Chem. Soc., Chem. Commun.* **1984**, 998.

[4] Garcia-Espana, E.; Micheloni, M.; Paoletti, P.; Bianchi, A. *Gazz. Chim. Ital.* **1985**, 115.

[5] Wieghardt, K.; Tolksdorf, J.; Hermann, W. *Inorg. Chem.* **1985**, *24*, 1230.

[6] Schneider, R.; Riesen, A.; Kaden, T. A. *Helv. Chim. Acta* **1985**, *68*, 53.

[7] Linking by N,N′ bridges of NS_2O rings (Bulkowski, J. E.; Burk, P. L.; Ludmann, M. F.; Osborne, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498) and of NO_3 rings (Calverly, M. J.; Dale, J. *J. Chem. Soc., Chem. Commun.* **1981**, 684) has also been reported.

[8] Barefield, E. K.; Chueng, D.; Van Derveer, D. G.; Wagner, F. *J. Chem. Soc., Chem. Commun.* **1981**, 302.

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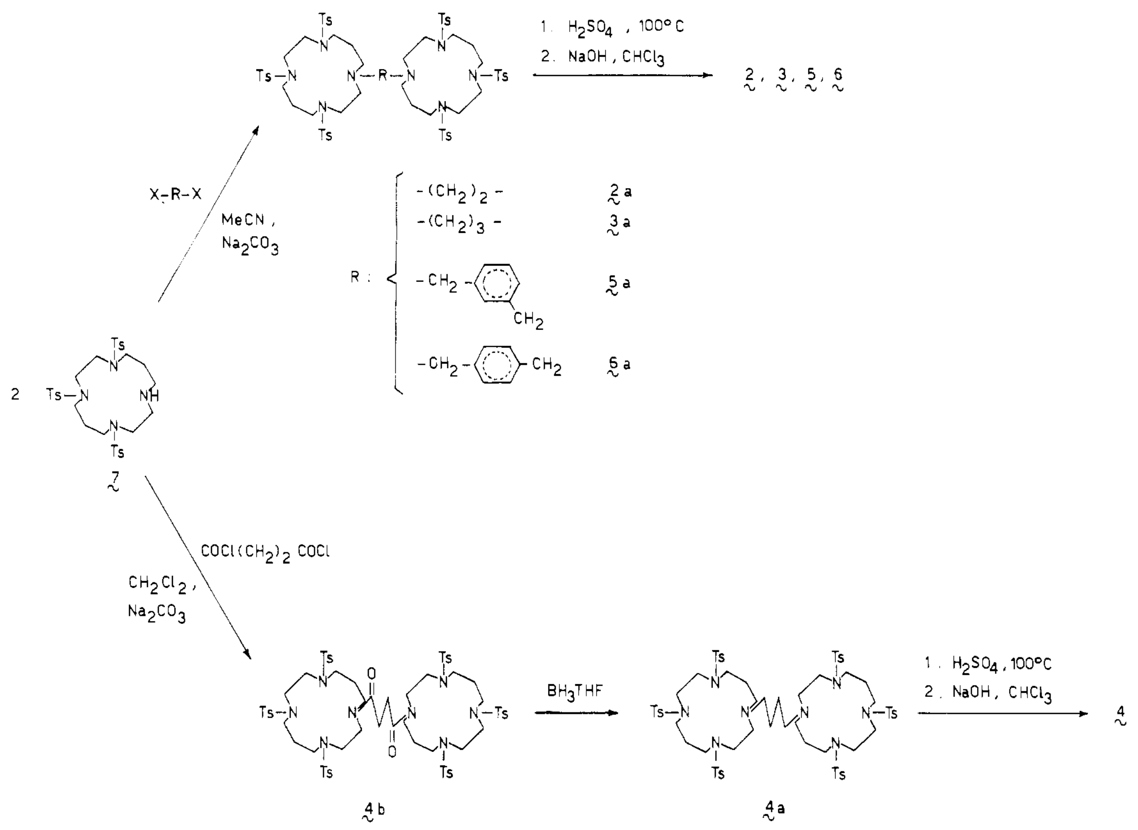
Scheme I



complex, especially resistant toward demetalation. The redox activity of the encircled metal ion is very often emphasized due to the macrocyclic coordination, which promotes the access to otherwise unstable oxidation states.[13] Thus, bis(macrocyclic) complexes may behave as two-electron-redox agents in solution. Due to the aliphatic linkage, any nonelectrostatic effect between the metal centers is excluded. Therefore, homodimetallic bis(macrocyclic) complexes represent ideal models for the study of mutual electrostatic effects in two-center redox systems.

We report here a novel family of N,N′-bis(macrocycles) (**2**–**6**, Chart I) appropriately designed for the investigation of the redox activity in solution of pairs of 3d metal ions. In these systems, two cyclam molecules (**1**, the most favorable framework for incorporation of 3d metal ions) are linked together through nitrogen atoms by a carbon chain, whose nature and length can be varied through the synthesis. Previous studies on monometallic single-ring complexes have shown that coordination by cyclam makes possible the +2/+3 redox change of nickel and copper complexes.[13] In this work we describe an electrochemical investigation on the stepwise two-electron oxidation of dinickel(II) and dicopper(II) complexes of bis(macrocycles) **2**–**6**. Mutual effects on the redox behavior are interpreted in terms of the electrostatic model, with a special reference to the influence of the distance between the redox-active centers.

Experimental Section

Synthesis of Bis(macrocycles). The synthetic route to ligands **2**–**6** is outlined in Scheme I.

Synthesis of *N,N′,N″*-Tritosylcyclam (7). *N,N′,N″*-Tritosylcyclam ($\mathrm{Ts_3}$cyclam, **7**) was obtained through direct reaction of cyclam (**1**) with tosyl chloride. It was observed that the above reaction performed with a 3:1 molar ratio of tosyl chloride/cyclam yielded a mixture containing both $\mathrm{Ts_3}$cyclam (35%) and $\mathrm{Ts_4}$cyclam (35%), the balance being mainly one out of the three isomers of $\mathrm{Ts_2}$cyclam. However, the separation of $\mathrm{Ts_3}$cyclam proved to be difficult; we found that a better procedure is to perform the tosylation reaction according to a 2:1 molar ratio of tosyl chloride/cyclam, which avoids formation of the undesired $\mathrm{Ts_4}$cyclam (vide infra).

A solution of tosyl chloride (22.8 g, 0.12 mol) in chloroform (800 mL) was added dropwise to a solution of cyclam (**1**; 12.0 g, 0.06 mol) in chloroform (400 mL) and triethylamine (50 mL) kept at 40 °C, over a period of 5 h. After the mixture stood at room temperature overnight, water (100 mL) was added with stirring. The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The solid residue was dissolved in hot methanol (60 mL) and cooled to room temperature. As the solution stood, white crystals of **7**·H_2O separated (13.0 g, 32%). The product could be recrystallized from hot toluene, yielding the anhydrous mono(toluene) adduct **7**·tol (tol = toluene). A second crop of the tritosyl derivative was obtained by evaporating to dryness the mother liquor of the first crop, dissolving the resulting sticky oil in chloroform (400 mL) and triethylamine (30 mL), and adding to the solution tosyl chloride (4.6 g, 0.024 mol) dissolved in chloroform (200 mL) at 40 °C in 1 h. Standard workup of this solution gave **7**·H_2O (9.9 g, 24%).

Synthesis of the Tosylated Bis(macrocycles) 2a, 3a, 5a, and 6a. A suspension of **7**·tol (5.0 g, 6.6 mmol), 1,2-bis(tosyloxy)ethane (1.2 g, 3.2 mmol),[14] and anhydrous sodium carbonate (1 g) was refluxed in dry acetonitrile for 4 days. After the mixture was cooled to room temperature, water (20 mL) and dichloromethane (40 mL) were added with stirring. The organic layer was separated, dried over anhydrous sodium sulfate, and filtered. To the dichloromethane solution was added methanol up to incipient precipitation. As the solution stood, white crystals of **2a**·H_2O separated (2.6 g, yield 58%).

An analogous procedure using 1,3-bis(tosyloxy)propane and *p*- and *m*-dibromoxylene yielded **3a**, **5a**, and **6a**, respectively, in 35–60% yields.

Synthesis of 2, 3, 5, and 6. Deprotection of the hexatosyl bis(macrocycles) to give the free ligands **2**, **3**, **5**, and **6** was carried out as previously described.[14]

Synthesis of 4. Repeated attempts performed with 1,4-bis(tosyloxy)butane as bridging segment failed to give the hexatosylated bis(macrocycle) **4a**, only the monosubstituted 1-(tosyloxy)-4-(tritosyl-

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(9) Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Seghi, B. *J. Chem. Soc., Chem. Commun.* **1982**, 1166.

(10) Fabbrizzi, L.; Forlini, F.; Perotti, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 807.

(11) Buttafava, A.; Fabbrizzi, A.; Perotti, A.; Poggi, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 3917.

(12) Fabbrizzi, L.; Montagna, L.; Poggi, A.; Kaden, T. A.; Siegfried, L. *Inorg. Chem.* **1986**, *25*, 2671.

(13) Fabbrizzi, L. *Comments Inorg. Chem.* **1985**, *4*, 33.

(14) Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Poli, G.; Seghi, B. *Inorg. Chem.* **1986**, *25*, 1456.

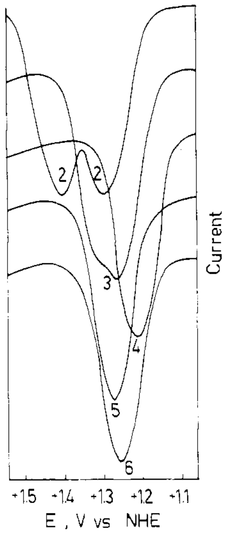

Figure 1. Differential pulse voltammetry (DPV) profiles obtained for 5 × 10^{-4} M solutions of $[Cu_2(bis(cyclam))](ClO_4)_4$ complexes in 70% $HClO_4$ (platinum-microsphere working electrode; pulse amplitude 10 mV; potential scan rate 2 mV s^{-1}). Numbers refer to bis(macrocycles) reported in Chart I.

cyclam)butane being obtained. This compound did not further react with an excess of **7**·tol in refluxing acetonitrile for 1 week nor in dimethylformamide at 140 °C for 3 days.

Thus, $(COClCH_2)_2$ was used as bridging segment. In particular, to a stirred solution of **7**·tol (6.5 g, 8.6 mmol) and triethylamine (4 mL) in dry dichloromethane (50 mL) was added a solution of succinyl dichloride (0.66 g, 4.3 mmol) dropwise at 0 °C. The solution was kept at room temperature for 2 h and then stirred with a concentrated solution of sodium carbonate (30 mL). The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated to dryness. The yellowish material was recrystallized from hot ethanol/water (95:5 v/v), giving the diamide **4b** as a white microcrystalline solid (5.4 g, 89%). A 1 M solution of BH_3 in tetrahydrofuran (20 mL) was added dropwise to a solution of **4b** (1.4 g, 1 mmol) in dry tetrahydrofuran (5 mL) at 0 °C. The resulting solution was refluxed for 8 h, cooled to room temperature, quenched with a water/methanol mixture (5:15 v/v), and evaporated to dryness. The residue was stirred in dichloromethane (20 mL) and filtered and the solution evaporated to dryness. The solid material, analyzed as **4a**·$2BH_3$, was dissolved in 96% sulfuric acid (2 mL) and heated to 100 °C for 3 days. Standard workup gave **4** (yield 55%).

Listings of melting points and analytical data for bis(macrocycles) **2**–**6** and their precursors are available as supplementary material.

Dinickel(II) and Dicopper(II) Complexes. Dimetallic complexes were obtained as microcrystalline precipitates (yellow-orange for nickel; purple-red for copper) by mixing ethanolic solutions of the ligand and of the metal perchlorate (1:2 molar ratio) and allowing to reflux for 30 min. The complexes, recrystallized from methanol, gave satisfactory C, H, N elemental analysis.

Electrochemistry. Voltammetric investigations were performed with an AMEL 472 apparatus, equipped with a Hewlett-Packard 7040 XY recorder. In general, the differential pulse voltammetry technique was employed, with a pulse potential of 10 mV. A conventional three-electrode cell, thermostated at 25 °C by a circulating water bath, was used. The working electrode was a platinum microsphere (1 mm diameter). A silver wire was used as pseudo reference electrode, which was calibrated vs. NHE through the Fe^{3+}/Fe^{2+} internal reference standard[15] in 70% $HClO_4$ solution measurements and vs. the Fc^+/Fc reference couple in nonaqueous solvents. Concentrated $HClO_4$ (Fluka purissimum p.A.) was used as supplied. Nonaqueous solvents were purified through distillation over CaH_2 and stored over molecular sieves under a nitrogen atmosphere. Tetraethylammonium tetrafluoroborate (Et_4NBF_4, Erba, polarographic grade) was used as supporting electrolyte in nonaqueous media.

Results

Voltammetric investigations have been performed, with a platinum-microsphere working electrode, (i) in concentrated perchloric acid solution (dicopper and dinickel complexes) and (ii) in nonaqueous media, MeCN, Me_2SO, DMF, etc. (dinickel complexes). Concentrated $HClO_4$ is a very special medium that permits formation of Cu^{III} tetraaza macrocyclic complexes stable at least in the time scale of the voltammetry experiment.[15] In contrast to the case for copper, trivalent nickel complexes are stable in aqueous acidic solution and in the most common nonaqueous solvents used in electrochemistry.[13]

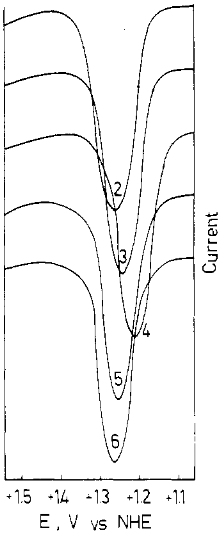

Figure 2. Differential pulse voltammetry (DPV) profiles obtained for 5 × 10^{-4} M solutions of $[Ni_2(bis(cyclam))](ClO_4)_4$ complexes in 70% $HClO_4$. Experimental conditions are as in Figure 1. Numbers refer to the bis(macrocycles) reported in Chart I.

Among voltammetric methods, the differential pulse voltammetry (DPV) technique was used, since it permits the greatest resolution of the signals associated with consecutive redox events, whose potentials are not very distant. In Figure 1 we report the DPV profiles obtained in the oxidation scan for 5 × 10^{-4} M solutions of $[Cu_2(\mathbf{2}–\mathbf{6})](ClO_4)_4$ complexes in concentrated $HClO_4$ solution. It can be seen that for the dinuclear species in which the metal centers are closer (ligand **2**), two distinct peaks are observed, the first one being assigned to the Cu^{II}/Cu^{III} oxidation process at one of the metal centers, the second one to be ascribed to the one-electron oxidation at the other metal center, according to the general mechanism

$$[M^{II}M^{II}L]^{4+} \rightleftharpoons [M^{III}M^{II}]^{5+} + e^- \qquad (1)$$

$$[M^{III}M^{II}]^{5+} \rightleftharpoons [M^{III}M^{III}]^{6+} + e^- \qquad (2)$$

From the difference of the peak potentials, Δp, the difference of the redox potentials associated with the half-reactions (2) and (1), $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$, can be evaluated, by using the work function obtained by Richardson and Taube.[16] When the aliphatic link between the two rings is lengthened by a $-CH_2-$ unit (bis(macrocycle) **3**), two peaks are still distinguishable in the DPV profile, but their separation is much smaller. Furthermore, for dicopper complexes in which the distance between metal centers is greater (ligands **4**, **5**, and **6**), the two peaks coalesce. In this case, the $\Delta E_{1/2}$ value can be calculated from the value of the width at the half-peak, $\delta_{1/2}$.[16] For dinickel complexes, in concentrated $HClO_4$ solution, even at the shortest ring-to-ring distance (ligand **2**), a single wide peak appears, whose width decreases with increasing separation of the two rings (Figure 2). For measurements in 70% $HClO_4$ solution, a pseudo reference electrode was used (a silver wire), which was calibrated with respect to the Fe^{3+}/Fe^{2+} internal reference couple and the measurement then converted to the H^+/H_2 scale by using the equation of Ciavatta.[17] $E_{1/2}(1)$ and $E_{1/2}(2)$ values and Δp, $\delta_{1/2}$, and $\Delta E_{1/2}$ parameters for the electrochemical investigation in 70% $HClO_4$ solution are reported in Table I. In the case of dinickel complexes, DPV investigation has been performed also in acetonitrile solution. Figure 3 reports

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(15) Bisi Castellani, C.; Fabbrizzi, L.; Licchelli, M.; Perotti, A.; Poggi, A. *J. Chem. Soc., Chem. Commun.* **1984**, 806.

(16) Richardson, O. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(17) Ciavatta, L. *Ann. Chim. (Rome)* **1980**, *70*, 551.

Table I. Electrochemical Parameters for the Two-Electron Stepwise Oxidation of $[M_2(\text{bis(cyclam)})](ClO_4)_4$ Complexes in 70% $HClO_4$ Solution at 25 °C

bis(cyclam)	Δp[a]	$\delta_{1/2}$[b]	$\Delta E_{1/2}$[c]	$E_{1/2}(1)$[d]	$E_{1/2}(2)$[e]	$-\Delta G^\circ_{el}$[f]
			M = Cu			
2	110		115	1.290	1.405	1.82
3		160	80	1.242	1.322	1.01
4		115	54	1.185	1.239	0.42
5		110	52	1.251	1.303	0.37
6		109	51	1.231	1.282	0.35
			M = Ni			
2		110	52	1.236	1.288	0.37
3		96	41	1.220	1.260	0.11
4		91	36	1.194	1.230	0
5		91	36	1.236	1.272	0
6		91	36	1.249	1.285	0

[a] Peak to peak difference in a DPV response, in mV (see Figures 1 and 2). [b] Half-peak width, in mV. [c] Values (in mV) obtained through the work functions $\Delta E_{1/2} = f(\Delta p)$ and $f(\delta_{1/2})$ outlines by Richardson and Taube.[16] [d] Half-wave potential value associated with the redox change (1), in V vs NHE. [e] Half-wave potential value associated with the redox change (2), in V vs NHE. [f] Electrostatic contribution, in kcal mol^{-1}, to the comproportionation equilibrium (3), $= 23.06(\Delta E_{el})$ (V) ($\Delta E_{el} = \Delta E_{1/2} - 0.0365$).

Table II. Electrochemical Parameters for the Two-Electron Stepwise Oxidation of $[Ni_2(\text{bis(cyclam)})](ClO_4)_4$ Complexes in MeCN Solution 0.1 M in Et_4NBF_4 at 25 °C[a]

bis(cyclam)	Δp	$\delta_{1/2}$	$\Delta E_{1/2}$	$E_{1/2}(1)$	$E_{1/2}(2)$	$-\Delta G^\circ_{el}$
2	90		100	0.755	0.855	1.48
3		133	66	0.697	0.763	0.69
4		113	54	0.687	0.732	0.42
5		109	50	0.720	0.770	0.35
6		109	50	0.735	0.785	0.35

[a] Column headings are as defined in Table I. Potential values are in V vs Fc^+/Fc.

the DPV profiles recorded for 5×10^{-4} M solutions of $[Ni_2(\mathbf{2}\text{–}\mathbf{6})](ClO_4)_4$ complexes in MeCN, made 0.1 M in Et_4NBF_4. In comparison to the case for the above-mentioned perchloric acid solutions, separation of the redox potentials for steps 1 and 2 appears large enough to disclose two well-distinguishable peaks for the shortest chain bis(cyclam) complex $[Ni_2(\mathbf{2})](ClO_4)_4$. As observed for the dicopper analogue in $HClO_4$ solution, lengthening the bridge between the two rings makes $\Delta E_{1/2}$ smaller and smaller and the two peaks coalesce into a single one. $\Delta E_{1/2}$ values for investigated dinickel complexes, calculated from Δp or $\delta_{1/2}$ parameters, are reported in Table II.

Discussion

Design of Ditopic Receptors for Redox-Active Metal Centers. The aim of this work was to evaluate electrostatic effects on the redox behavior of two metal centers at variable distance. Bis(macrocycles) represent the ideal ditopic receptors for this type of investigation. In fact, it is known that encircling of a 3d metal ion by a tetraaza macrocycle promotes its redox activity, making accessible oxidation states that are otherwise unstable (e.g. Ni^{III}, Cu^{III}).[13] Moreover, the distance between the two rings, i.e. between the two redox centers, in the dimetallic complex can be modulated by inserting a linking chain of appropriate length. We believe that the N,N′-linked bis(cyclam) molecules described here represent, among bis(macrocycles), the most appropriate receptors for redox studies on pairs of metal ions. In fact, the cyclam subunit guarantees the highest thermodynamic and kinetic stability of macrocyclic complexes, in particular permitting the easiest access to the trivalent state of nickel[18] and copper.[19]

It should be noted that a crucial intermediate for the synthesis of bis(macrocycles) is the selectively protected polyaza subunit to be linked. An elegant, but time consuming, multistep synthesis of the tritosylated isocyclam ring has been recently described.[20] In contrast, in this work, the protected subunit, Ts_3cyclam, is very simply prepared through reaction of cyclam with 2 equiv of TsCl: Ts_3cyclam is obtained in crystalline form in 32% yield. A further 24% is obtained by treating the mother liquor with additional TsCl. Furthermore, two Ts_3cyclam molecules are bridged through the unprotected secondary amine groups by reaction with the appropriate X–R–X segment (X = Br or OTs) to give molecules **2**, **3**, **5**, and **6**. However, bridging by the above procedure with a tetramethylene chain failed. Thus, ligand **4** was obtained through the reaction of Ts_3cyclam (2 equiv) with succinyl dichloride: the corresponding diamide was reduced with diborane. In any case, the hexatosylated bis(macrocycles) were deprotected through hydrolysis in concentrated sulfuric acid.

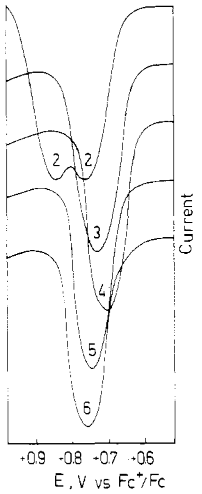

Figure 3. Differential pulse voltammetry (DPV) profiles obtained for 5×10^{-4} M solutions of $[Ni_2(\text{bis(cyclam)})](ClO_4)_4$ in MeCN (0.1 M Et_4NBF_4). Experimental conditions are as in Figure 1. Numbers refer to the bis(macrocycles) reported in Chart I.

Synthesis of the above family of N,N-linked bis(macrocycles) appears particularly convenient, essentially due to the ready availability of the Ts_3cyclam intermediate. In particular, Ts_3cyclam may open the route to many kinds of functionalized macrocycles, based on the privileged framework of cyclam. Applications in this sense are currently under investigation in our laboratories.

Valence-Scrambling Equilibria. A very interesting parameter obtained from the voltammetric investigations on the redox behavior of dimetallic bis(macrocyclic) complexes is $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$, which, due to the electrochemically reversible nature of the studied processes, approximates ΔE°. Moreover, ΔE° is related, according to $\Delta G^\circ = -nF(\Delta E^\circ)$, to the free energy change ΔG°_{com}, associated with the "valence scrambling" (or comproportionation equilibrium (3)).

$$[M^{III}M^{III}(L)]^{6+} + [M^{II}M^{II}(L)]^{4+} \rightleftharpoons 2[M^{III}M^{II}(L)]^{5+} \quad (3)$$

As outlined by Taube,[21] ΔG°_{com} can be split into two distinct contributions:

$$\Delta G^\circ_{com} = \Delta G^\circ_{stat} + \Delta G^\circ_{el} \quad (4)$$

ΔG°_{stat}, the statistical contribution ($=-RT \ln 4$), is always favorable and reflects the greater probability (by a factor of 4) associated with the formation of the mixed-valence species, compared to that for the $M^{III}M^{III}$ and $M^{II}M^{II}$ complexes in the left-hand side of eq 3 ($= 23.06 \times 36.5$ mV $= 0.842$ kcal mol^{-1}, at 25 °C).

ΔG°_{el}, the electrostatic contribution, is negative or nil and reflects the decrease of the electrostatic repulsion between metal

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(18) Bencini, A.; Fabbrizzi, L.; Poggi, A. *Inorg. Chem.* **1981**, *20*, 2544.

(19) Fabbrizzi, L.; Poggi, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2191.

(20) Hediger, M.; Kaden, T. A. *J. Chem. Soc., Chem. Commun.* **1978**, 14; *Helv. Chim. Acta* **1983**, *66*, 861.

(21) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

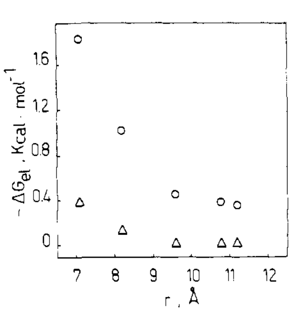

Figure 4. Electrostatic contribution to the comproportionation equilibrium (3), ΔG°_{el}, vs the calculated distance between metal centers, *r*, for dimetallic bis(cyclam) complexes in 70% $HClO_4$ solutions: (Δ) nickel complexes; (○) copper complexes. *r* values increase along the series of bis(macrocycles) **2**, **3**, **4**, **5**, and **6**.

centers in the bis(macrocyclic) complexes, which occurs during the comproportionation process (3). To justify this effect, it is useful to define an energy quantity for the electrostatic interaction, A_{el}

$$A_{el} = Ne^2/Dr \qquad (5)$$

where *N* is Avogadro's number, *e* the electron charge, *D* the dielectric constant of the medium, and *r* the distance between the metal centers. It should be noted that a repulsive electrostatic term of $13A_{el}$ (=(3 × 3)A_{el} + (2 × 2)A_{el}) is associated with the species on the left-hand side of the comproportionation equilibrium (3), whereas a repulsive term of $12A_{el}$ (=2(2 × 3)A_{el}) is associated with the species on the right-hand side of (3). Thus, the comproportionation equilibrium (3) involves a net reduction of the repulsive electrostatic energy by 1 A_{el} unit. This quantity (=332/(*D*[*r* (Å)]) kcal mol^{-1}) should equal the measured ΔG°_{el} value. It will be shown in the examples reported below that ΔG_{el} values may substantially differ from the calculated value of A_{el}, essentially due to the use of inappropriate values of the dielectric constant *D*. In any case, one would expect that ΔG°_{el} becomes more important (and consequently the peak separation in the DPV profile increases) with the decrease of both the dielectric constant, *D*, and the distance between metal centers, *r*.

Dicopper and Dinickel Complexes in Concentrated Perchloric Acid. Effect of the Metal-to-Metal Distance and of the Stereochemistry of the Redox Center. In Figure 4 ΔG°_{el} values associated with the comproportionation equilibria for dinickel and dicopper complexes, which have been calculated from values in Table I, are plotted against the metal-to-metal distance, *r*. *r* values have been calculated by assuming that each bis(macrocyclic) complex adopts an anti conformation, in order to keep the metal centers at the greatest possible distance.[22] According to such an arrangement, all the bonds of the joining chain (including the M–N coordinative bonds) should lie in the same plane. Thus, *r* values have been trigonometrically calculated by using the standard values for C–C and C–N distances and 2.00 Å for the M–N distance and 109.5° for the bond angles. Corresponding values (Å) are as follows: **2**, 7.09; **3**, 8.19; **4**, 9.57; **5**, 10.77; **6**, 11.19.[23]

Figure 4 shows that, for both dinickel and dicopper complexes, ΔG°_{el} values decrease with increasing *r* distance in a roughly hyperbolic mode. This behavior is fully consistent with the electrostatic repulsion model. In the case of nickel ΔG°_{el} is particularly small even at the shortest ring-to-ring distance (bis(macrocycle) **2**), and, with the increasing length of the bridge, further decreases to a nearly constant value. It may be surprising that the comproportionation equilibrium for dicopper complexes, at a given *r* distance, involves a much larger electrostatic contribution than that for dinickel complexes, in spite of the apparent similarity of the two metals. To make this point clear, it is useful to consider the comproportionation equilibria in their stereochemical details. As a matter of fact, there is a great deal of experimental evidence on the corresponding monometallic single-ring complexes (with cyclam and related ligands) that (1) Ni(III) and Cu(II) complexes exhibit a trans-elongated octahedral stereochemistry and (2) Ni(II) and Cu(III) complexes present a square stereochemistry.[13] Therefore, the comproportionation equilibria should be better written as

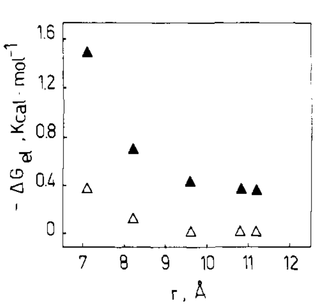

Figure 5. Electrostatic contribution to the comproportionation equilibrium (3), ΔG°_{el}, vs the calculated distance between the metal centers, *r*, for dinickel bis(cyclam) complexes: (Δ) 70% $HClO_4$ solution; (▲) MeCN solution. *r* values increase along the series of bis(macrocycles) **2**, **3**, **4**, **5**, and **6**.

$$[Ni^{III}(H_2O)_2,Ni^{III}(H_2O)_2(L)]^{6+} + [Ni^{II},Ni^{II}(L)]^{4+} \rightleftharpoons 2[Ni^{III}(H_2O)_2,Ni^{II}(L)]^{5+} \qquad (6)$$

$$[Cu^{III},Cu^{III}(L)]^{6+} + [Cu^{II}(H_2O)_2,Cu^{II}(H_2O)_2(L)]^{4+} \rightleftharpoons 2[Cu^{III},Cu^{II}(H_2O)_2(L)]^{5+} \qquad (7)$$

It seems reasonable to admit that apically coordinated water molecules quench to some extent the electrical charge of the metal ion. Thus, the square Ni^{II} and Cu^{III} metal centers should display an effective charge greater than diaquo octahedral Ni^{III} and Cu^{II} centers. Quantification of this effect is not possible. However, in order to make a purely qualitative test of the above hypothesis, let us assume that *trans*-diaquo coordination causes a reduction of the formal electrical charge by 0.5 unit. This leads to a calculated electrostatic term much larger for the dicopper complex equilibrium (7), 2.25 A_{el}, than for the dinickel complex, $0.25A_{el}$. In any case, even when a different charge decrement is used (larger or smaller than 0.5), it will be found that the electrostatic effect calculated for the dicopper system comproportionation equilibrium is greater than that calculated for the dinickel system. These conclusions are consistent with the experimental evidence that valence-scrambling equilibria involving dicopper complexes are characterized by a greater (in absolute value) electrostatic contribution ΔG°_{el} and by a larger $\Delta E_{1/2}$ value than those of dinickel complexes displaying the same metal-to-metal distance. Moreover, the above model also accounts for the greater dependence of ΔG°_{el} upon *r* for dicopper than for dinickel complexes.

Dinickel Complexes in Acetonitrile Solution and Other Nonaqueous Media. Effect of the Dielectric Constant. Figure 5 shows a plot of ΔG°_{el} values associated with the dinickel comproportionation equilibrium in MeCN solution vs. the calculated distance between the metal centers. In this case too, ΔG°_{el} values decrease with *r* according to the expected hyperbolic mode and are much more sensitive to *r* than observed in $HClO_4$ solution. In particular, it is to be noted that, at a given ring-to-ring distance, the electrostatic term is much more important in MeCN solution than in the $HClO_4$ medium previously considered. This could be simply explained on the basis of Coulomb's law considering that MeCN has a dielectric constant much smaller than the aqueous perchloric acid solution. The above observation prompted us to consider the comproportionation equilibrium for the dinickel complexes with the shortest chain bis(macrocycle) **2** in various media (made 0.1 M in Et_4NBF_4) having different values of *D*. The corresponding ΔG°_{el} values are plotted in Figure 6 vs the dielectric constant values. Points in the figure do not seem to be meaningfully correlated and in any case are very scattered with respect to the

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(22) Recent X-ray diffraction studies[6] of two dinickel(II) bis(macrocyclic) complexes in which two isocyclam rings are linked by an ethylenic and by a *p*-xylyl bridge indeed show this arrangement, the metal centers being at the longest possible distance.

(23) Metal-to-metal distances crystallographically determined[6] for the low-spin dinickel(II) bis(macrocyclic) complexes are 7.05 Å for the system having the ethylenic chain (to be compared to **2**) and 11.56 Å for the system having the *p*-xylyl bridge (to be compared to **6**).

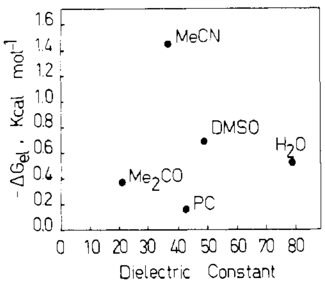

Figure 6. Electrostatic contribution to the valence-scrambling equilibrium (3) ($\Delta G°_{el}$) for the $[Ni_2(\mathbf{2})](ClO_4)_4$ complex vs the dielectric constant of the medium.

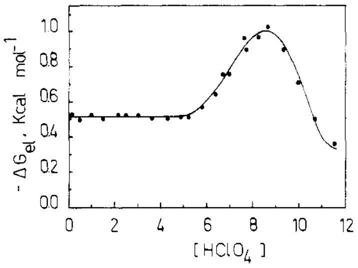

Figure 7. Electrostatic contribution, $\Delta G°_{el}$, to the comproportionation equilibrium of $[Ni_2(\mathbf{2})](ClO_4)_4$ in $HClO_4$ solutions of varying concentration. The solid line represents the best-fitting curve obtained through a nonlinear least-squares procedure.

hypothetical hyperbolic curve expected on the basis of the electrostatic model. This indicates that bulk values of D are absolutely not appropriate to describe short-range phenomena, and individual values of D that reflect the local solvation mode in the considered bis(macrocyclic) complex system should be used.

Inadequacy of macroscopic values of D to interpret electrostatic interactions in solution has been pointed out by several authors long ago in the study of "proton scrambling" equilibria of diprotic systems (dicarboxylic acids[24,25] and diammonium ions).[26,27]

$\Delta G°_{el}$ Values as a Probe To Investigate Local Dielectric Phenomena. If bulk values of D cannot explain the trend of $\Delta G°_{el}$, it may occur, conversely, that investigation of $\Delta G°_{el}$ values can disclose and help in understanding some unexpected local dielectric behavior.

For instance, studying the comproportionation equilibrium involving the dinickel complexes with the shortest chain bis(macrocycle) **2** in aqueous $HClO_4$ solution, in the range 0.1–11.6 M, we have discovered a peculiar dependence of $\Delta G°_{el}$ on the acid concentration (See Figure 7). In particular, $\Delta G°_{el}$ maintains a constant value up to a $HClO_4$ concentration of 6 M. At a 7 M $HClO_4$ level$\Delta G°_{el}$ increases (thus D decreases) to reach a maximum value (which is twice the value in diluted solution) at 9 M $HClO_4$. Following this, a sharp decrease is observed (see Figure 7). A tentative explanation is the following: under diluted conditions, the strongly hydrophilic H^+ ion progressively added subtracts water molecules from the solvent; however, at these concentration levels, the hydration shell around the dimetallic complexes remains intact. At higher acid concentration H^+ and, to a lesser extent, ClO_4^- ions compete with the dimetallic complexes for the solvating water molecules. At this stage, desolvation of the complexes occurs and this reduces the dielectric shielding of the metal centers, making $\Delta G°_{el}$ increase steeply. On the other hand, with increasing concentration of $HClO_4$, the density of ClO_4^- anions becomes so high that they may approach closely the dimetallic species and possibly interpose between the metal centers, thus exerting a direct shielding of the proximate metal charges.[28] This effect becomes predominant at a $HClO_4$ concentration $\geq$9 M, where $\Delta G°_{el}$ starts to decrease steeply. Note that at this concentration level, with use of the ionic lattice model, an average ClO_4^-–ClO_4^- distance of 5.7 Å, comparable to that estimated for the metal-to-metal distance, can be calculated.

Therefore, the peculiar dependence of $\Delta G°_{el}$ on the concentration of $HClO_4$ seems to result from two independent contributions: (i) desolvation of the dimetallic system due to the competing effect of the H^+ ions and (ii) ion-pair formation. The maximum of the peak in Figure 7 corresponds to the highest interference of the two effects.

Electrostatic and Ligand Effects on the Oxidation of the First Metal Center. In the previous sections we have considered the $\Delta E_{1/2}$ quantity, and not the individual values of $E_{1/2}(1)$ and $E_{1/2}(2)$, associated with the oxidation processes involving the first and second metal center, respectively. Inspection of values reported in Tables I and II shows that for a given series of dimetallic systems in a given medium (e.g. $[Cu_2(\mathbf{2}\text{–}\mathbf{6})](ClO_4)_4$ in 11.56 M $HClO_4$) $E_{1/2}(1)$ values vary over a substantial range of potential (up to 105 mV) and are larger or equal to those observed for the reference mononuclear system (complexes with cyclam **1** or with the N-monomethylated cyclam ligand Mecyclam (**8**), which, as for the subunits of the bis(macrocycles) reported here, contains three secondary nitrogen atoms and a tertiary one).[29] For all the considered series of complexes, $E_{1/2}(1)$ exhibits the more positive value, i.e., the M^{II}/M^{III} oxidation process is most difficult, with the shortest linking chain macrocycle **2** and decreases with the increasing number of methylene groups of the bridge (**3** and **4** bis(macrocycles)), to approach the value observed with the reference mononuclear system.[28]

The above trend can be rationalized in terms of electrostatic arguments: oxidation of the first metal center (charge increase from 2+ to 3+) is made difficult by the presence of the adjacent dipositive cation, and on the other hand, the repulsive effect decreases when the distance from the adjacent cation is progressively increased.

Surprisingly, the longest bridging chain systems **5** and **6** present $E_{1/2}$ values more positive than those of **3** and **4** complexes, in which the metal-to-metal distance is considerably shorter. However, it should be considered that the nature of the substituent on the donor atoms may substantially alter the redox behavior of the encircled metal ion. In particular, the presence of the xylyl group may reduce the donor strength of the tertiary nitrogen atom, compared to that with simple aliphatic substituents, due to a combination of steric and inductive effects. Moreover, it is a general rule that a decrease of the ligand field makes more difficult oxidation processes involving d metal ions. Therefore, in the oxidation of the first metal center in $[M^{II}_2(\mathbf{5},\mathbf{6})]^{4+}$ complexes, the advantage due to the longer distance of the adjacent charge is more than compensated by the reduction of the donor strength of the tetraaza subunit. Exotic effects of this latter type cancel in the case of the valence-scrambling equilibria discussed before, which are solely controlled by the electrostatic term.

Conclusions

In this work we have tried to interpret the redox behavior of species containing two chemically equivalent redox centers according to a simple electrostatic model. The interpretation is forcedly qualitative since we are not in the position to quantify

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(24) Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506.

(25) Westheimer, F. H.; Kirkwood, J. G. *J. Chem. Phys.* **1938**, *6*, 513.

(26) Paoletti, P.; Walser, R.; Vacca, A.; Schwarzenbach, G. *Helv. Chim. Acta* **1970**, *54*, 243.

(27) Fabbrizzi, L.; Paoletti, P.; Zobrist, M. C.; Schwarzenbach, G. *Helv. Chim. Acta* **1973**, *56*, 670.

(28) At very high concentrations of $HClO_4$ it may also occur that ClO_4^- ions replace water molecules in the axial sites of the octahedrally distorted Ni^{III} and Cu^{II} complexes, to exert a more direct charge quenching. According to this hypothesis, eq 6 and 7 should be appropriately rewritten. It should be noted that apical coordination by ClO_4^- ions rather than by H_2O molecules reinforces the interpretation of the different electrostatic contribution of $\Delta G°_{el}$ to comproportionation equilibria 6 and 7, based on the reduction of the electrical charge of the metal centers.

(29) $E_{1/2}(M^{III}/M^{II})$ (V vs NHE, in 11.56 M $HClO_4$: $[Ni(\mathbf{2})]^{3+/2+}$, 1.04; $[Ni(\mathbf{8})]^{3+/2+}$, 1.19; $[Cu(\mathbf{1})]^{3+/2+}$, 1.16; $[Cu(\mathbf{8})]^{3+/2+}$, 1.22. $E_{1/2}(M^{III}/M^{II})$ (V vs Fc^+/Fc, in MeCN 0.1 M in Et_4NBF_4): $[Ni(\mathbf{1})]^{3+/2+}$, 0.600; $[Ni(\mathbf{8})]^{3+/2+}$, 0.696. Values were taken from ref 30.

(30) Ciampolini, M.; Fabbrizzi, L.; Licchelli, M.; Perotti, A.; Pezzini, F.; Poggi, A. *Inorg. Chem.* **1986**, *25*, 4131.

the electrical charge of the redox-active metal ions. In particular, it has been shown that its effective value varies with the nature of the metal and with its stereochemical arrangement. Moreover, the bulk value of the dielectric constant of the medium is absolutely not appropriate to describe the shielding effect exerted by the solvational molecules. In particular, in strongly saline solutions, the ions of the so-called "inert electrolyte" may substantially modify the solvation state of the dimetallic system and seriously affect its redox behavior. The only parameter of Coulomb's law whose role seems to be accounted for, in a quantitative sense, is the distance between metal centers. Due to the stretched arrangement of the joining chain, its value can be calculated on the basis of molecular models.

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Registry No. **1**, 295-37-4; **2**, 110078-38-1; **2a**, 110078-39-2; **3**, 110078-40-5; **3a**, 110078-41-6; **4**, 110078-42-7; **4a**, 110078-43-8; **4b**, 110078-48-3; **5**, 110078-44-9; **5a**, 110078-45-0; **6**, 110078-46-1; **6a**, 110078-47-2; **7**, 104395-69-9; $[Cu_2(\mathbf{2})](ClO_4)_4$, 110095-31-3; $[Cu_2(\mathbf{2})]^{5+}$, 110095-60-8; $[Cu_2(\mathbf{2})]^{6+}$, 110095-50-6; $[Cu_2(\mathbf{3})](ClO_4)_4$, 110095-33-5; $[Cu_2(\mathbf{3})]^{5+}$, 110095-61-9; $[Cu_2(\mathbf{3})]^{6+}$, 110095-51-7; $[Cu_2(\mathbf{4})](ClO_4)_4$, 110095-35-7; $[Cu_2(\mathbf{4})]^{5+}$, 110095-62-0; $[Cu_2(\mathbf{4})]^{6+}$, 110095-52-8; $[Cu_2(\mathbf{5})](ClO_4)_4$, 110095-37-9; $[Cu_2(\mathbf{5})]^{5+}$, 110095-63-1; $[Cu_2(\mathbf{5})]^{6+}$, 110095-53-9; $[Cu_2(\mathbf{6})](ClO_4)_4$, 110095-39-1; $[Cu_2(\mathbf{6})]^{5+}$, 110095-64-2; $[Cu_2(\mathbf{6})]^{6+}$, 110095-54-0; $[Ni_2(\mathbf{2})](ClO_4)_4$, 110095-41-5; $[Ni_2(\mathbf{2})]^{5+}$, 110095-65-3; $[Ni_2(\mathbf{2})]^{6+}$, 110095-55-1; $[Ni_2(\mathbf{3})](ClO_4)_4$, 110095-43-7; $[Ni_2(\mathbf{3})]^{5+}$, 110095-66-4; $[Ni_2(\mathbf{3})]^{6+}$, 110095-56-2; $[Ni_2(\mathbf{4})](ClO_4)_4$, 110095-45-9; $[Ni_2(\mathbf{4})]^{5+}$, 110095-67-5; $[Ni_2(\mathbf{4})]^{6+}$, 110095-57-3; $[Ni_2(\mathbf{5})](ClO_4)_4$, 110095-47-1; $[Ni_2(\mathbf{5})]^{5+}$, 110095-68-6; $[Ni_2(\mathbf{5})]^{6+}$, 110095-58-4; $[Ni_2(\mathbf{6})](ClO_4)_4$, 110095-49-3; $[Ni_2(\mathbf{6})]^{5+}$, 110095-69-7; $[Ni_2(\mathbf{6})]^{6+}$, 110095-59-5; $TsOCH_2CH_2OTs$, 6315-52-2; $TsOCH_2CH_2CH_2OTs$, 5469-66-9; TsCl, 98-59-9; $BrCH_2$-*m*-C_6H_4–CH_2Br, 626-15-3; $BrCH_2$-*p*-C_6H_4–CH_2Br, 623-24-5; $COCl(CH_2)_2COCl$, 543-20-4.

Supplementary Material Available: A table containing melting points and analytical data (C, H, N) of the bis(macrocycles) **2–4** and of their protected precursors (1 page). Ordering information is given on any masthead page.

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Lewis-Base Adducts of Group 11 Metal(I) Compounds. 32. Steric Effects in the 2:1 Adducts of (2-Methylphenyl)diphenylphosphine with Copper(I) Halides

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Solid-state ^{31}P NMR spectra, far-infrared spectra, and single-crystal X-ray structure determinations have been recorded for (2-methylphenyl)diphenylphosphine (PPh_2-*o*-tol) and its mononuclear 2:1 adducts with copper(I) halides, $(PPh_2\text{-}o\text{-tol})_2CuX$. The solid state ^{31}P NMR spectrum of the ligand shows a single sharp resonance at −18 ppm with respect to 85% H_3PO_4. The spectra of the 2:1 adducts show two sets of overlapping asymmetric quartets for the chloride and bromide and a single broad quartet for the iodide, indicating the presence of at least two crystallographically distinct ligands in the first two compounds and one in the third. Average chemical shift values (ppm) are as follows: Cl, −11; Br, −11; I, −15. The asymmetry in the line spacing for each quartet is consistent with a trigonal coordination geometry around the copper atom. Far-infrared spectra of each of the metal complexes in the range 50–400 cm^{-1} show strong bands that are assigned to terminal metal–halogen stretching vibrations: Cu–Cl, 290 cm^{-1}; Cu–Br, 220 cm^{-1}; Cu–I, 200 cm^{-1}. The parent ligand crystallizes in the monoclinic space group $P2_1/c$ with a = 10.713 (5) Å, b = 8.726 (5) Å, c = 16.573 (6) Å, β = 90.77 (3)°, and Z = 4. All three copper structures crystallize in the monoclinic space group $C2/c$. The Cl and Br structures are isomorphous with one complete molecule of $(PPh_2\text{-}o\text{-tol})_2CuX$ comprising the asymmetric unit. For X = Cl, a = 22.413 (15) Å, b = 16.034 (4) Å, c = 19.092 (2) Å, β = 107.04 (4)°, and Z = 8; for X = Br, a = 22.348 (7) Å, b = 16.033 (8) Å, c = 19.526 (5) Å, β = 108.73 (2)°, and Z = 8. However, for X = I, a = 18.665 (5) Å, b = 10.006 (2) Å, c = 19.764 (5) Å, β = 115.29 (2)°, and Z = 4, with the two ligands related by symmetry and the Cu–I bond sited on the 2-fold rotation axis. For X = Cl, Cu–P, Cu–P, Cu–X, and P–Cu–P = 2.241 (2) Å, 2.257 (2) Å, 2.205 (2) Å, and 126.96 (7)° respectively; for X = Br, the values are 2.240 (2) Å, 2.255 (2) Å, 2.336 (1) Å, and 127.89 (7)°, respectively; and for X = I, Cu–P, Cu–I, and P–Cu–P = 2.255 (1) Å, 2.507 (1) Å, and 126.36 (7)°, respectively. Both Cu–P and Cu–X distances are similar to the corresponding values for $(PPh_3)_2CuX$ compounds. However, as a consequence of changes in steric profile, the conformational structure of each ligand about the Cu–P bonds with respect to Cu–X is significantly different.

Introduction

Reaction of copper(I) halides, CuX, with tertiary organophosphine bases, PR_3, gives a wide range of products of variable stoichiometry and molecular structure. Most structural studies have been reported for compounds of 1:1 stoichiometry, $[PR_3CuX]_n$, and here the stellaquadrangula[2] or "cubane" structure is most common, crystallographic data being reported for a wide range of bases with differing steric and electronic characteristics including PEt_3 with X = Cl,[3] Br,[3] and I;[4] $PMePh_2$ with X = I;[5] PPh_3 with X = Cl,[6] Br,[7] and I,[8] and $P(t\text{-}Bu)_3$ with X = Br.[9] For PPh_3 and X = Br and I, a change of solvent results in the crystallization of the alternative "step" tetramer.[10] For the ligands, $P(chx)_3$ (chx = cyclohexyl) with X = Cl and $P(mes)_3$ (mes = mesityl) with X = Br, dimeric $[PR_3CuX]_2$[11] and monomeric $[PR_3CuX]$[12] structures, respectively, are obtained. By contrast,

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(1) (a) University of Auckland. (b) University of Western Australia. (c) Griffith University.

(2) Noren, B.; Oskarsson, A. *Acta Chem. Scand. Ser., A* **1985**, *A39*, 701.

(3) Churchill, M. R.; DeBoer, B. G.; Mendak, S. J. *Inorg. Chem.* **1975**, *14*, 2041.

(4) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1899.

(5) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 3267.

(6) Clayton, W. R; Shore, S. G. *Cryst. Struct. Commun.* **1973**, *2*, 605; Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1065.

(7) Barron, P. F.; Dyason, J. C.; Engelhardt, L. M.; Healy, P. C.; White, A. H. *Inorg. Chem.* **1984**, *23*, 3766.

(8) Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; Patrick, V. A.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 831.

(9) Goel, R. G.; Beauchamp, A. L. *Inorg. Chem.* **1983**, *22*, 395.

(10) Dyason, J. C.; Engelhardt, L. M.; Pakawatchai, C.; Healy, P. C.; White, A. H. *Aust. J. Chem.* **1985**, *38*, 1243 and references therein.

(11) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1979**, *18*, 166.

(12) Alyea, E. C.; Ferguson, G.; Malito, J.; Ruhl, B. L. *Inorg. Chem.* **1985**, *24*, 3720.