(10) on Ru(3), the atom most weakly bonded to P(1), semibridge to Ru(4) and Ru(5) respectively, the two metals that form the shortest bonds to the phosphide.[25] Such behavior suggests that the phosphide atom may contribute a greater share of its 5-electron donor capacity to Ru(4) and Ru(5).

We have previously noted that in **2**, a 46-electron cluster, there is an activated P–Ph group. The synthesis of **1** from **2** can then be viewed as resulting from the facile loss of phenyl groups from **2** as benzene[26] and subsequent condensation. Since the unsaturated cluster **2** is readily accessible from the 48-electron complex $Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-PPh}_2)$ via thermal, photochemical, or Me_3NO initiation, the strategy of benzene elimination from μ-hydrido, μ-diphenylphosphido complexes may well be generally applicable to the synthesis of cluster-bound phenylphosphides (PPh) or phosphides. We are exploring the wider implications of this suggestion.

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Registry No. **1**, 85134-96-9; **2**, 82055-65-0; C_6H_6, 71-43-2.

Supplementary Material Available: Listings of atomic positions (Table I), anisotropic thermal parameters, (Table II), bond lengths and angles (Table III), and structure factor amplitudes for $Ru_5(CO)_{16}(\mu_5\text{-P})(\mu\text{-PPh}_2)\cdot 2C_6H_6$ (28 pages). Ordering information is given on any current masthead page.

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[25] The angles Ru(3)–C(8)–O(8) and Ru(3)–C(10)–O(10) are 159.8 (3) and 155.5 (3)°. The Ru(4)–C(8) and Ru(5)–C(10) distances are 2.578 (9) and 2.487 (9) Å.

[26] Benzene has been identified as a product of the thermolysis of **2** by GC. When the thermolysis of **2** is carried out in heptane, samples of **1** crystallized from the reaction mixture contain benzene of crystallization in the lattice.

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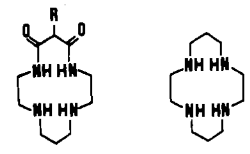
The Deprotonated Amido vs. the Amino Group in the Stabilization of Coordinated Trivalent Copper and Nickel Cations. An Electrochemical Evaluation

Sir:

The tetraaza macrocycle *dioxocyclam* (**1a**) is able to incorporate in aqueous solution the copper(II) ion with simultaneous deprotonation of the two amido groups.[1] The resulting (dioxocyclamato)copper(II) complex in water undergoes chemical or anodic one-electron oxidation which occurs at a moderately positive potential, 0.65 V vs. SCE, to give an authentic Cu(III) species, which persists in water for hours.[2] This is a unique behavior for tetraaza macrocycles in spite of their renowned ability to stabilize unusually high and otherwise unstable oxidation states of the incorporated transition-metal cation.[3] In fact the fully saturated analogue of **1a**, *cyclam* (**2**), which forms water-stable Ni^{III},[4] Ag^{II},[5] and Ag^{III}[5] complexes, gives a Cu(III) species only in anhydrous acetonitrile, which persists in solution only in the time scale of the cyclic voltammetry experiment ($E_{1/2}$ for the Cu^{II}/Cu^{III} redox change 0.99 V vs. Fc^+/Fc, in MeCN with 0.1 M Et_4NBF_4).[6] The stabilizing effect on the trivalent copper exerted by the deprotonated NCO group (amido or peptido) had been previously demonstrated in the broad class of copper polypeptide complexes prepared in Margerum's laboratory.[7] At this stage, it seemed interesting to compare the electrode potential for the Cu^{II}/Cu^{III} redox couple in cyclam and dioxocyclamato complexes, in order to evaluate directly the effect of replacing amine groups by deprotonated amido groups in the stabilization of trivalent copper. However, such a direct comparison was prevented by the fact that the (dioxocyclamato)copper(II) complex is soluble in water but insoluble in most organic solvents such as acetonitrile.



1a: R = H
1b: R = $CH_2C_6H_5$
2

In this connection, we have prepared the macrocycle **1b** (benzyldioxocyclam), in which, in order to increase the solubility of the complex in organic solvents, a lipophilic benzyl group has been inserted in the carbon framework of dioxocyclam, in such a position that cannot alter the donor properties of the ligand. **1b** has been prepared according to Tabushi's procedure[8] by aminolytic condensation of diethyl 3-benzylmalonate and 1,4,8,11-tetraazaundecane in refluxing absolute ethanol (3 days, 5×10^{-2} mol dm^{-3}). A soluble (benzyldioxocyclamato)copper(II) species can be obtained both in water and in acetonitrile. The complex was prepared in situ in the chosen solvent from equimolecular amounts of Cu^{2+} and **1b** in the presence of base. In aqueous solution the formation of the (benzyldioxocyclamato)copper(II) complex was monitored through pH titration by standard base of **1b** (H_2L) in the presence of Cu^{+2} in a 1:1 molar ratio. Complexation occurs with simultaneous release of two protons (from the amido groups) in the pH range 4–5.5. The constant for the equilibrium $Cu^{2+} + H_2L \rightleftharpoons CuL + 2H^+$, calculated from the computer analysis of the titration data[9] (0.25 log unit), is slightly lower than found for *dioxocyclam* (0.44). Aqueous (benzyldioxocyclamato)copper(II) presents an absorption band in the d–d spectrum centered at 20 100 cm^{-1} with an extinction coefficient of 69 $dm^3\ mol^{-1}\ cm^{-1}$ (for (dioxocyclamato)copper(II) ν(d–d) = 19 850 cm^{-1}, ϵ = 89 $dm^3\ mol^{-1}\ cm^{-1}$). CV studies performed with a carbon-paste electrode in 0.1 M KCl solution indicated that the (benzyldioxocyclamato)copper(II) complex undergoes a one-electron reversible oxidation process (to the Cu^{III} complex) at an $E_{1/2}$ value (0.66 V vs. SCE) very close to that found for the dioxocyclamato analogue under the same conditions (0.65 V vs. SCE).

The (benzyldioxocyclamato)copper(II) complex can be obtained in acetonitrile solution by mixing equimolecular amounts of **1b** and copper(II) acetate. Addition of excess ligand or base (triethylamine) did not alter the intensity and energy of the d–d band, indicating that the macrocyclic com-

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[1] Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1979**, 325.

[2] Fabbrizzi, L.; Poggi, A. *J. Chem. Soc., Chem. Commun.* **1980**, 646.

[3] Melson, G. A. "Coordination Chemistry of Macrocyclic Compounds"; Plenum Press: New York, 1979.

[4] Haines, R. I.; McAuley, A. *Inorg. Chem.* **1980**, *19*, 719.

[5] Barefield, E. K.; Mocella, M. T. *Inorg. Chem.* **1973**, *12*, 2829.

[6] Zanello, P.; Seeber, R.; Cinquantini, A.; Mazzocchin, G. A.; Fabbrizzi, L. *J. Chem. Soc., Dalton Trans.* **1982**, 893.

[7] Bossu, F. P.; Margerum, D. W. *Inorg. Chem.* **1977**, *16*, 1210.

[8] Tabushi, I.; Taniguchi, Y.; Kato, H. *Tetrahedron Lett.* **1977**, 1049.

[9] The computer program MINIQUAD (Sabatini, A.; Vacca, A.; Gans, G. *Talanta* **1974**, *21*, 53) was used. log *K* values for stepwise protonation are as follows: for **1b**, log K_1 = 9.35 ± 0.02, log K_2 = 5.70 ± 0.07; for **1a**, log K_1 = 9.52 ± 0.02, log K_2 = 5.79 ± 0.05. All the equilibrium data refer to 0.1 M $NaClO_4$ solutions, at 25 °C.

plex was already completely formed. CV investigation, performed with a platinum electrode in 0.1 M Et_4NBF_4 solution, showed a quasi-reversible profile with an $E_{1/2}(Cu^{II}/Cu^{III})$ value of 0.15 V vs. Fc^+/Fc. Consider that $E_{1/2}$ for the same redox change with the complex of the tetraamine analogue (cyclam) is 0.99 V.[6] The extraordinarily large difference (19.4 kcal mol^{-1}) expresses quantitatively the stabilization effect of trivalent copper caused by replacement of two amine nitrogen atoms by two deprotonated amido groups.

The behavior of the corresponding nickel complexes is surprising. Comparison between cyclam and benzyldioxocyclamato complexes in acetonitrile cannot be done, as the (benzyldioxocyclamato)nickel(II) complex in MeCN solution gives on oxidation at a platinum or gold electrode a highly distorted, poorly reversible CV profile. However, comparison between the two types of macrocycles can be made in water, where both cyclam and dioxocyclamato Ni^{II} complexes are stable. The $E_{1/2}(Ni^{II}/Ni^{III})$ values were calculated from CV profiles obtained with a platinum electrode in 3 M KCl.[10] They are as follows: cyclam, 0.47 V vs. SCE; dioxocyclamato, 0.51 V vs. SCE. Thus in this case the amine/deprotonated amide replacement would involve destabilization of Ni^{III}, even if this is very moderate. Probably, this comparison is not totally correct, if one considers that the Ni(III) chromophore, low-spin d^7, has an octahedral stereochemistry and, in the experimental conditions used, the two apical positions should be occupied by chloride ions. It may be that the tripositive cyclam complex may profit from axial ligation to a larger extent than the formally monopositive dioxocyclamato complex. CV experiments performed in aqueous 7 M $NaClO_4$,[10] where axial coordination must be in any case much less intense, gave a reverse order of $E_{1/2}(Ni^{II}/Ni^{III})$ values: cyclam, 0.81 V; dioxocyclamato, 0.61 V.[11] However, the advantage of the dioxocyclamato group in the stabilization of Ni^{III} remains moderate, with respect to the case for Cu^{III}. This state of affairs can be explained by considering the following: (i) the dinegatively charged dioxocyclamato ligand (as well as its benzyl derivative) is remarkably stronger than cyclam as an electron donor; (ii) the Cu^{II}/Cu^{III} redox change (d^9, square planar/d^8, square planar) profits from a large CFSE contribution, 12.28*Dq* (to which the further effect due to the increase of the cationic charge is to be added); (iii) the Ni^{II}/Ni^{III} redox change (low-spin d^8, square planar/low-spin d^7, octahedral) involves a destabilization in terms of CFSE (−6.56*Dq*), which may be eventually compensated by the contribution due to the increase of the charge.

Present results indicate that the easier attainment of trivalent copper, when coordinated by deprotonated amido groups rather than by amine nitrogen atoms, is essentially a ligand field effect and does not derive merely from the reduction of the formal electrical charge of the complex. Finally, it can be concluded that cations in unusually high oxidation states, whose formation profits from large CFSE contributions, can be stabilized by coordination of negatively charged nitrogen atoms such as amido or peptido groups. In this connection, other molecules in which nitrogen atoms have substituents that may promote deprotonation should be envisaged by coordination chemists as ligands potentially versatile in the stabilization of unusually high oxidation states of transition-metal ions.

Registry No. Cu, 7440-50-8; Ni, 7440-02-0; (dioxocyclamato)copper(II), 72547-88-7; (dioxocyclamato)copper(III), 75674-95-2; (benzyldioxocyclamato)copper(II), 80386-15-8; (benzyldioxocyclamato)copper(III), 85185-69-9; (dioxocyclamato)nickel(II), 78737-53-8; (dioxocyclamato)nickel(III), 85185-70-2; (cyclam)nickel(II), 46365-93-9; (cyclam)nickel(III), 66199-97-1; (benzyldioxocyclamato)nickel(II), 85185-71-3; diethyl benzylmalonate, 607-81-8; 1,4,8,11-tetraazaundecane, 4741-99-5.

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(10) A high concentration of the inert electrolyte was used in order to obtain a quasi-reversible behavior in the case of the (dioxocyclamato)nickel(II) complex. Δp of the CV profile, at a potential scan rate of 40 mV s^{-1}, was 95 mV for both 3 M KCl and 7 M $NaClO_4$ solutions.

(11) The $E_{1/2}$ values refer to a unbuffered neutral solution. Ni^{II} tetraaza macrocyclic complexes may exhibit hydrolytic activity in aqueous solution.[12] A tendency for hydrolysis can be quenched on addition of acid. $E_{1/2}(Ni^{II}/Ni^{III})$ for the cyclam complex in a 7 M $NaClO_4$ solution made 1 M in strong acid is 0.84 V, i.e. 0.03 V higher than in the neutral solution; this value should correspond to the Ni^{II}/Ni^{III} redox change uncomplicated by hydrolysis. A same procedure could not be employed for the dioxocyclamato system, since the (dioxocyclamato)nickel(II) complex is labile and decomposes on addition of acid. It is probable that the 1+ (dioxocyclamato)nickel(III) species, due to the lower charge, is a weaker acid than the cyclam analogue; in this case the $E_{1/2}(Ni^{II}/Ni^{III})$ value for the process uncomplicated by hydrolysis should be closer to the value found in neutral solution. However, also in the less favorable case the difference between $E_{1/2}$ values for cyclam and dioxocyalamato complexes would be increased only by 0.03 V. This small correction does not alter the substance of the comparison and the conclusion to be drawn on the different behaviors of nickel and copper complexes.

(12) Cohen, H.; Kirschenbaum, L. J.; Zeigerson, E.; Jaacobi, M.; Fuchs, E.; Ginzburg, G.; Meyerstein, D. *Inorg. Chem.* **1979**, *18*, 2763.

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