creased to only 350–420 mV. This reversal in substituent effects and decrease in $\Delta E_{1/2}$ for the metalloporphyrins may be due to an electron–electron repulsion in the dianions that is much stronger in the case of porphyrins than for phthalocyanines, where the conjugated system is more delocalized.

In summary, this study has shown that cyano-substituted phthalocyanines may be easily reduced by four single-electron transfers, which occur at very low potentials. The properties of these compounds are very close to those of tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ), thus suggesting the use of cyano-substituted phthalocyanines as charge-transfer complexes.

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Registry No. $ZnPc(CN)_8$, 76228-28-9; $[ZnPc(CN)_8]^{-\cdot}$, 85335-42-8; $[ZnPc(CN)_8]^{2-}$, 85335-43-9; $[ZnPc(CN)_8]^{3-\cdot}$, 85335-44-0; $[ZnPc(CN)_8]^{4-}$, 85354-79-6; $CuPc(CN)_8$, 75810-80-9; $[CuPc(CN)_8]^{-\cdot}$, 95155-95-6; $[CuPc(CN)_8]^{2-}$, 95155-96-7; $[CuPc(CN)_8]^{3-\cdot}$, 95155-97-8; $[CuPc(CN)_8]^{4-}$, 95155-98-9; $H_2Pc(CN)_8$, 76221-26-6; $[H_2Pc(CN)_8]^{-\cdot}$, 95191-81-4; $[H_2Pc(CN)_8]^{2-}$, 95191-82-5; $[H_2Pc(CN)_8]^{3-\cdot}$, 95191-83-6; $[H_2Pc(CN)_8]^{4-}$, 95191-84-7; Au, 7440-57-5; Hg, 7439-97-6; Pt, 7440-06-4.

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Investigation into the Linkage Isomerism of the Sulfamidate Group: A Quantitative Assessment Using ESCA

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The ESCA spectra of several transition-metal complexes containing sulfamidate as a ligand are described. The difference in the N_{1s} and the S_{2p} binding energies, $\Delta(N_{1s}-S_{2p})$, is used to show whether or not the sulfamidate is coordinated via nitrogen. The advantages of this method over infrared analysis are discussed. It is shown that when linkage isomerism of sulfamidate occurs, the ESCA technique is capable of quantitative determination of the relative amounts of the isomers.

Introduction

Infrared and Raman spectroscopic evidence suggests that the sulfamidate ligand in $K_3[M(NH_2SO_3)Cl_5]$ (M = Rh, Ir, Os), in $K_2[Pd(NH_2SO_3)_2Cl_2]$, and in $K_2[Pt(NH_2SO_3)_2X_2]$ (X = Cl, Br) is bonded to the metal through nitrogen.[2] This is also the case for $[Ru(NH_3)_5(NH_2SO_3)]^{2+}$.[3] In aqueous alkaline solution, the visible spectra and acidity constants for $[Co(NH_3)_5(NH_2SO_3)]^{2+}$ show that the sulfamidato ligand is nitrogen bonded,[4] while in acid solution hydrolysis kinetic data and changes in the visible spectra suggest that N- and O-bonded linkage isomerism of the sulfamidato ligand occurs.[5] However, the O-bonded isomer could not be isolated. The infrared spectra for a series of first-row transition-metal sulfamidates show that both O and N coordination occurs.[6] It was suggested that monodentate coordination of the sulfamidate group occurs via oxygen while nitrogen coordination indicates the presence of a chelating or a bridging ligand, except in the case of Cr(III) or Cu(II), where simple monodentate coordination through the nitrogen occurs.[6]

In the complexes the infrared evidence is based on (i) shifts observed in the N–H bands at 3350, 3270, and 1550 cm^{-1}; (ii) shifts in the ν(N–S) band, although this tends to be sensitive to N coordination alone; and (iii) shifts in the SO_3 modes that, in practice, are limited to a broadening effect on the bands involved. Although this proves quite adequate for most of the complexes, there is difficulty in complexes containing ammine or amine ligands.[6] Thus, the mode of sulfamidate coordination in ethylenediamine complexes could not be positively identified, as the relevant bands of the sulfamidato group overlap with those of the ethylenediamine ligand in the infrared spectrum.[6] As the determination of the mode of coordination depends largely on the shifts in the N–H bands, a complication can arise from the possibility of hydrogen-bonding effects, especially in aqua complexes. Furthermore, interconversion of the N- and O-bonded isomers can occur, and the preparative route often determines the isomer or isomers formed.[6] Then, in cases where both isomers are present, a quantitative determination of their relative amounts is difficult by infrared techniques.

ESCA has been used previously to determine the mode of coordination of an ambidentate ligand in a series of metal sulfoxide complexes.[7] More recently, complexes of sulfur-substituted oxopryimidines have been examined by using ESCA, and coordination of the thio group has been confirmed and ambidentate behavior postulated.[8,9]

In this paper we show that by using ESCA it is possible to determine the mode of coordination for the sulfamidato group, from a comparison of the binding energies of the ligand core electrons, in a series of transition-metal sulfamidato complexes and some complexes containing ethylenediamine, pyridine, and ammonia ligands. The isomeric ratios are also determined by a comparison of the corresponding peak intensities, in those cases where both linkage isomers are present.

Experimental Section

Sulfamidic acid was obtained commerically from BDH Chemicals and used without further purification. Metal sulfamidates were prepared by the addition of metal carbonates or freshly prepared metal hydroxides to sulfamidic acid.[6] Sodium sulfamidate was prepared by the exact neutralization of sulfamidic acid using AnalaR grade sodium hydroxide, followed by the partial evaporation of the water.[15] Some second- and third-row transition-metal sulfamidates were prepared by similar methods using the metal hydroxides (Rh(III), Cd(II)) or the oxide (Ag(I)). Palladium sulfamidate complexes was prepared from $PdCl_2$ by the stoichiometric addition of 2 mol of sulfamidic acid. The resulting solution was heated at 60 °C for 1 h, filtered, and then evaporated to near dryness on a steam bath. Recrystallization of all samples from water or water/methanol solutions gave products shown in Tables I and II.

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Table I. ESCA Data and Mode of Coordination of the Sulfamidate Ligand for Some First-Row Transition-Metal Complexes

complex	binding energies, eV $[\Delta(N_{1s}-S_{2p})]$		% N isomer
NH_2SO_3H	232.5		
NH_2SO_3Na		230.9	0
$[Ni(NH_2SO_3)_2(H_2O)_4]^a$		231.2	0
$[Ni(NH_2SO_3)_2(H_2O)_x]^b$	233.2	231.3	40 ± 10
$[Ni(NH_2SO_3)_2(H_2O)_2]^c$	233.1		100
$[Ni(NH_2SO_3)_2(H_2O)_x]^d$	233.1	231.2	70
$[Co(NH_2SO_3)_2(H_2O)_4]^a$		230.9	0
$[Co(NH_2SO_3)_2(H_2O)_2]^c$	233.0		>90
$[Co(NH_2SO_3)_2(H_2O)_x]^d$	232.8	230.9	30 ± 5
$[Zn(NH_2SO_3)_2(H_2O)_4]^a$		230.8	0
$[Zn(NH_2SO_3)_2(H_2O)_x]^b$	233.0	231.1	45 ± 5
$[Zn(NH_2SO_3)_2(H_2O)_2]^c$	233.1		100
$[Zn(NH_2SO_3)_2(H_2O)_4]^{e,f}$	233.1		100
$[Cu(NH_2SO_3)_2(H_2O)_2]^{a,f}$	233.5	231.5	35
$[Cu(NH_2SO_3)_2(H_2O)_x]^{b,f}$	232.9	230.6	85
$[Cu(NH_2SO_3)_2(H_2O)_x]^{d,f}$	233.1	231.2	20
$[Cu(NH_2SO_3)_2(H_2O)_3]^{a,g}$	232.8		100
$[Cu(NH_2SO_3)_2(H_2O)_x]^{b,g}$	232.8	231.8	>90
$[Cu(NH_2SO_3)_2(H_2O)_x]^{d,g}$	232.8	231.1	70 ± 5
$[Cr(NH_2SO_3)_2(H_2O)_3]$		230.9	0

[a] Freshly prepared sample. [b] Heated sample, $2 \geqslant x \geqslant 4$. [c] Heated sample, analysis obtained. [d] Heated sample, several years old, $2 \geqslant x \geqslant 4$. [e] Heated sample, redissolved in water and recrystallized. [f] Sample from copper carbonate preparation. [g] Sample from copper perchlorate preparation. (In the copper complexes the value of x in the samples marked *b* or *d* was always close to 2.)

Table II. ESCA Data and Mode of Coordination of the Sulfamidate Ligand for Some Second- and Third-Row Transition-Metal Complexes

complex formula	binding energies, eV $[\Delta(N_{1s}-S_{2p})]$		% N isomer
$[Rh(NH_2SO_3)_3(H_2O)_3]\cdot H_2O$		231.0	0
$[Cd(NH_2SO_3)_2(H_2O)_2]$		231.1	0
$[Ag(NH_2SO_3)(H_2O)]$	...	230.9	0
$[Pd(NH_2SO_3)_2]$	...	231.4	0

Table III. ESCA Data and Mode of Sulfamidate Coordination for Ammonia, Pyridine, and Ethylene Complexes of Ni(II), Co(II), and Cu(II)

complex formula	binding energies, eV $[\Delta(N_{1s}-S_{2p})]$		% N isomer
$[Co(NH_3)_5(NH_2SO_3)](ClO_4)_2$		231.1	0
$[Co(NH_3)_5(NHSO_3)]Cl$	232.9	231.4	>85
$[Ni(NH_2SO_3)_2(en)_2]$		231.0	0
$[Ni(en)_3](NH_2SO_3)_2$		231.4	0
$[Cu(NH_2SO_3)_2(en)_2]$		231.4	0
$[Ni(NH_2SO_3)_2(py)_4]$		231.2	0
$[Co(NH_2SO_3)_2(py)_4]$		231.2	0
$[Cu(NH_2SO_3)_2(py)_2]$		231.3	0

Analyses, except for the heated samples marked in the table, were within 1% in all cases.

The complexes were heated to constant weight in a drying oven at 180 °C. These were kept in a desiccator until they were transferred to the ESCA instrument. Other samples were sealed in ampules and used much later.

ESCA spectra of powdered samples mounted on the ESCA sample probe tip with double-sided tape were obtained on a McPherson ESCA-36 spectrometer using Mg α X-radiation. The pressure in the sample chamber and the analyzer region was less than 5×10^{-8} torr. The spectrometer was calibrated from the separation between the $Au_{4f_{7/2}}$ (binding energy 83.8 eV) and the $Ag_{3d_{3/2}}$ (binding energy 368.2 eV) photoelectron lines.[10]

In the cases where absolute binding energies were determined, residual hydrocarbon, originating in the spectrometer, was allowed to build up on the samples to a level sufficient to obtain good C_{1s} spectra. This line was used as a binding energy reference (285.0 eV).[10]

Overlapping component peaks were deconvoluted and integrated by using a peak-fitting computer routine.[11]

Results and Discussion

The complexes studied are listed in Tables I–III, together with the relevant ESCA data.

Sulfamidic acid exists in the solid state as the zwitterion,[12] $^+NH_3SO_3^-$. The N_{1s} binding energy (401.7 eV) is very similar to that found in some zwitterionic amino acids,[13] while the S_{2p} binding energy (169.2 eV) is consistent with the binding energy of some highly oxidized forms of sulfur.[14] In the sulfamidate ion, as in sodium sulfamidate, there is a net loss of one proton accompanied by a reduction in the N_{1s} binding energy to 400.1 eV. Ionization does not result in a change in the S_{2p} or O_{1s} binding energies. These atoms are remote from the site of ionization, and apparently ionization is not accompanied by a significant change in the charge distribution of the SO_3 group.

Previously, we showed that only the N_{1s} binding energy changes with the mode of the ligand binding.[15] The fact that the S_{2p} band does not change is to be expected as the sulfur is not directly involved in coordination to the metal, and it is therefore convenient to use as an internal reference for the binding energies. This is done by expressing the data for the samples studied here as the difference between the N_{1s} and the $S_{2p_{3/2}}$ binding energy in each compound, $\Delta(N_{1s}–S_{2+_{3/2}})$. (The S_{2p} level is preferred over the O_{1s} level as a number of the compounds reported here are aqua complexes, in which several chemically different oxygen environments are present. This gives rise to broadening of the O_{1s} bands in the ESCA spectra of these samples, with an increased uncertainty in defining the peak center. The compounds all have a single environment for sulfur, so the S_{2p} band remains sharp.) The advantages of this approach have been pointed out before.[7] Briefly, effects on the binding energies due to (a) different metal ion oxidation state, (b) molecular geometry, and especially (c) sample charging are effectively eliminated by an internal reference. Effects due to sample charging can give rise to uncertainties in determining absolute binding energies. Table I gives the observed values for $\Delta(N_{1s}–S_{2p})$, for the first-row transition-metal sulfamidates studied, together with the results for sodium sulfamidate and sulfamidic acid. In most instances the quoted results are mean values obtained from two or three samples. Table II contains the results for the other transition-metal sulfamidates, while Table III gives the $\Delta(N_{1s}–S_{2p})$ values for some ammine, pyridine, and ethylenediamine complexes of nickel, copper, and cobalt.

(a) First-Row Transition-Metal Sulfamidates. From Table I, the value of $\Delta(N_{1s}–S_{2p})$ observed for sodium sulfamidate is consistently repeated in the tetraaquabis(sulfamidato) complexes of nickel(II), cobalt(II), and zinc(II), in which sulfamidate coordination occurs through one of the oxygen atoms.[6] As both nitrogen and sulfur are remote from the site of coordination, changes in electron distribution in the sulfamidate group brought about by complex formation are insufficient to give a change in $\Delta(N_{1s}–S_{2p})$. Changes in the O_{1s} binding energy on complexation either are too small to be detected or are unobservable due to the large number of oxygen atoms in several chemical environments in these compounds. It is not possible therefore to distinguish oxygen-coordinated sulfamidate ligand from sulfamidate ion by ESCA.

However, it is possible to distinguish situations in which coordination occurs through the nitrogen. Thus, when the nickel, cobalt, and zinc tetraaquabis(sulfamidato)metal(II) complexes are heated, 2 mol of water are lost, the colors of the complexes

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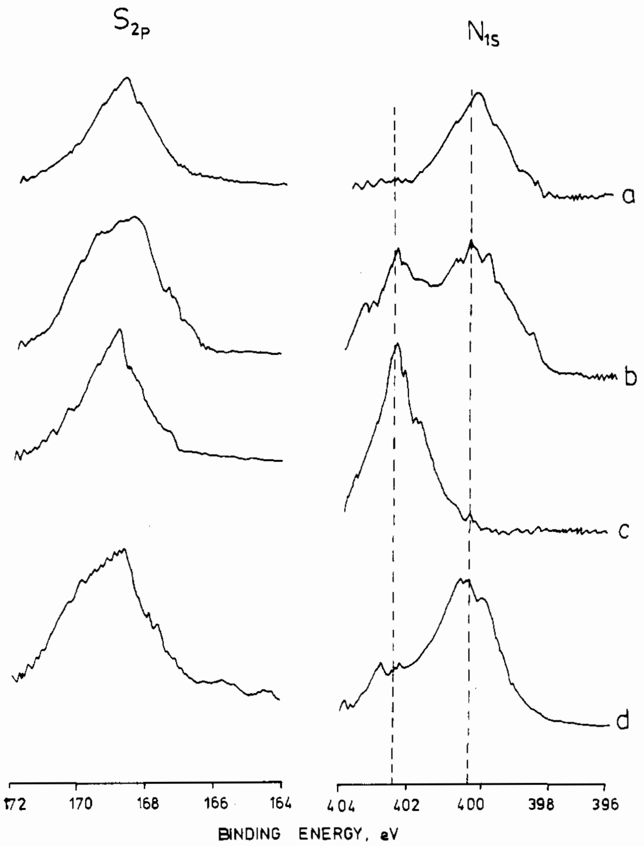

Figure 1. S_{2p} and N_{1s} ESCA spectra of nickel sulfamidates: (a) tetraaquabis(sulfamidato)nickel(II); (b) tetraaquabis(sulfamidato)nickel(II), heated to 160 °C; (c) diaquabis(sulfamidato)nickel(II); (d) diaquabis(sulfamidato)nickel(II), left for several days in the atmosphere.

change, and a new N_{1s} peak emerges at higher binding energy, with $\Delta(N_{1s}-S_{2p}) = 233.0 \pm 0.2$ eV. For the cobalt and nickel complexes, this N_{1s} component becomes apparent after heating to about 150 °C and is the only component observed after 2 mol of water have been removed at a temperature above 200 °C. The zinc complex requires heating to 170 °C for 24 h before the new N_{1s} peak is the only component observed. The increase in the N_{1s} binding energy arises from a decrease in electron density on nitrogen, due to coordination via nitrogen to the metal ion. The resulting value for $\Delta(N_{1s}-S_{2p})$ (233.0 ± 0.2 eV) is similar to that observed in sulfamidic acid (232.6 eV). It is not apparent from the ESCA spectra whether the sulfamidate group in these diaqua complexes is monodentate and coordinated through nitrogen, viz. O_3SH_2N-, or bidentate and coordinated through both nitrogen and oxygen. In the latter case the sulfamidate either could be acting as a bridging ligand or could be forming a four-membered chelating ring with a single metal ion. The participation of nitrogen as a site of coordination is, however, readily detected from the ESCA spectra, as is apparent in Figure 1.

Reversion of the nitrogen-coordinated isomers back to their original form occurs for the nickel and cobalt diaqua complexes on exposure to moisture. Figure 1 shows the ESCA spectra for tetraaquabis(sulfamidato)nickel(II) (**1a**), a sample heated to about 160 °C (**1b**), and diaquabis(sulfamidato)nickel(II) (**1c**) together with a sample of **1c** run after a few days in the atmosphere (**1d**). A complete change back to the isomer with no nitrogen coordination eventually occurs. In sealed ampules the reversion takes place slowly. Six-year samples of the nickel(II) and cobalt(II) retained 70% and 30%, respectively, of the nitrogen-bound isomer when stored in this way. On the other hand the sulfamidato ligands in diaquabis(sulfamidato)zinc(II) remain coordinated through the nitrogen, even when the complex is recrystallized from water. This implies an extremely stable complex, and/or a high activation energy for the reversion process.

Sulfamidate coordination in triaquatris(sulfamidato)chromium(III) does not involve nitrogen, as evidenced by the single N_{1s} peak at $\Delta(N_{1s}-S_{2p}) = 230.9$ eV. In the previous assignment of nitrogen coordination in this complex, the possibility of N–H frequency shifts due to hydrogen bonding was suggested. The ESCA results imply that such hydrogen bonding does indeed complicate the interpretation of the infrared spectra for this complex.

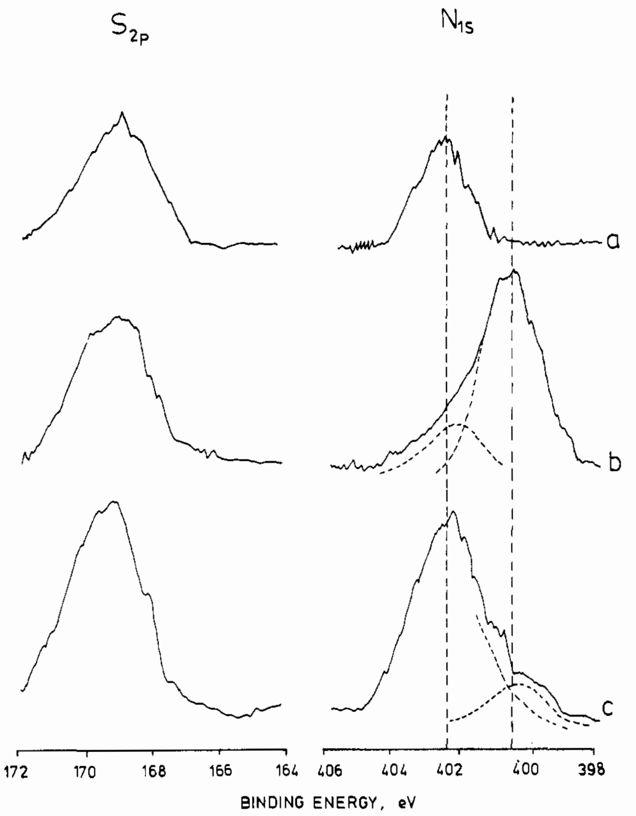

Figure 2. S_{2p} and N_{1s} ESCA spectra of copper sulfamidates: (a) triaquabis(sulfamidato)copper(II), prepared from copper perchlorate; (b) diaquabis(sulfamidato)copper(II), prepared from copper carbonate; (c) diaquabis(sulfamidato)copper(II), prepared from copper carbonate and heated to about 180 °C.

Diaquabis(sulfamidato)copper(II) prepared from different starting materials yields different products, identifiable in the ESCA spectra shown in Figure 2. When the reaction solution is neutral or only slightly acidic, as with $Cu(ClO_4)_2$, protonation of the amino nitrogen is unlikely and nitrogen coordination would be favored. The ESCA spectrum of the resulting complex (Figure 2a) shows a single nitrogen peak having $\Delta(N_{1s}-S_{2+}) = 232.8$ eV, indicative of the nitrogen-bound isomer. In more acidic conditions such as those using sulfamidic acid and copper carbonate, the amino group is protonated and thus unfavorable as a binding ligand. Nitrogen coordination then becomes less competitive, and the N_{1s} spectrum of the complex formed in this case shows two bands at $\Delta(N_{1s}-S_{2p}) = 233.0$ and 231.2 eV. The first of these corresponds to sulfamidato ligands in which nitrogen coordination occurs, while the other arises from ligands in which nitrogen coordination is absent. The relative intensities of these two bands indicate that in about 15% of the sulfamidate ligands nitrogen coordination is involved.

There is some difficulty in interpreting the results of the effect of heat on the copper complexes, as they tend to form copper sulfate at elevated temperatures[16] (the other product being ammonia). A heated sample of the complex prepared from copper perchlorate shows an unusual $\Delta(N_{1s}-S_{2p})$ of 231.8 eV, which may indicate some decomposition. This isomer was shown previously to be less stable than the corresponding complex prepared from copper carbonate.[6] However, with this proviso it can be seen that, on heating, a small amount of the oxygen-bound complex is formed, although the nitrogen-bound isomer still predominates.

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The complex prepared from copper carbonate follows more closely the behavior of other first-row metal complexes in that, on heating, the proportion of nitrogen-bound component is increased at the expense of the oxygen isomer.

(b) Other Metal Sulfamidates. The only bands observed in the N_{1s} ESCA spectra of the remaining metal sulfamidate complexes (Table II) have values of $\Delta(N_{1s}-S_{2p})$ (231.1 ± 0.2 eV) representitive of sulfamidate ligands in which nitrogen coordination does not occur.

(c) Complexes of Metal Sulfamidates. Studies of the mode of sulfamidate coordination in complexes containing other ligands such as ammine, ethylenediamine, and pyridine further demonstrate the usefulness of ESCA as a technique for quantitative inorganic analysis (Table III). Infrared studies of the complexes with ethylenediamine ligands were complicated because of the overlapping of bands in the N–H regions.[6] However, the ESCA spectra clearly show a single N_{1s} peak with $\Delta(N_{1s}-S_{2p}) = 231.2 \pm 0.2$ eV. Nitrogen in a sulfamidato ligand coordinated to the metal through nitrogen should have a binding energy some 2 eV higher, and this should be evident as a shoulder on the high binding energy side of the N_{1s} band. Simulated N_{1s} spectra consisting of two components separated by 2 eV and having relative intensities of 6 (tris(ethylenediamine)) to 2 (sulfamidato) show that such a shoulder would be readily distinguishable. It can be concluded that the sulfamidato ligand is not coordinated via nitrogen in these complexes. However, it is not possible to distinguish between oxygen coordination (as presumably in $[Ni(en)_2(NH_2SO_3)_2]$) and ionic sulfamidate (as in $[Ni(en)_3](NH_2SO_3)_2$).

The ESCA spectrum of $[Co(NH_3)_5(NH_2SO_3)]^{2+}$ shows a single N_{1s} component with $\Delta(N_{1s}-S_{2p}) = 231.1$ eV, so coordination of the sulfamidate through nitrogen does not occur, although this was suggested as the most likely isomeric form in aqueous solutions.[4] When the doubly deprotonated ligand $(NHSO_3)^{2-}$ is used, coordination through the nitrogen predominates. In this case the nitrogen is a strong Lewis base and is therefore a much more attractive site for coordination than the oxygen.

The ESCA data for the complexes containing pyridine indicate that the sulfamidate ligand is not coordinated through nitrogen. This agrees with earlier conclusions on the mode of coordination for the nickel and cobalt complexes, but not for the copper complex.[6]

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Dicopper(II) Complex of the Large Polyazacycloalkane 1,4,7,10,13,16,19,22-Octaazacyclotetracosane (bistrien). Synthesis, Crystal Structure, Electrochemistry, and Thermodynamics of Formation

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The large macrocycle 1,4,7,10,13,16,19,22-octaazacyclotetracosane (bistrien) was synthesized. The eight basicity constants and the stability constants of the dinuclear complexes $[Cu_2(bistrien)]^{4+}$, $[Cu_2(bistrien)H_2]^{6+}$, and $[Cu_2(bistrien)OH]^{3+}$ were determined by potentiometry at 25 °C in 0.5 mol dm^{-3} $NaClO_4$. The formation enthalpy of $[Cu_2(bistrien)]^{4+}$ was determined by batch microcalorimetry. The most important species, $[Cu_2(bistrien)]^{4+}$, is extremely stable ($\log k = 36.63$) and exothermic ($-\Delta H° = 39.0$ kcal mol^{-1}), indicating that all nitrogen atoms are involved in the coordination to the metal ions. The stability of the hydroxo species $[Cu_2(bistrien)OH]^{3+}$ is high, and its magnetic susceptibility in solution shows metal–metal interaction. Crystals of the compound $[Cu_2(bistrien)Cl_2](ClO_4)_2$ are monoclinic, space group $P2_1/m$, with $a = 11.811$ (3) Å, $b = 11.352$ (3) Å, $c = 11.385$ (3) Å, $\beta = 99.11$ (4)°, and $Z = 2$. Refinement of the atomic parameters by least squares gave a final R factor of 0.080 ($R_w = 0.070$) for 1340 unique reflections with $F_o > 2\sigma(F_o)$. The structure consists of centrosymmetric binuclear Cu_2(bistrien) units held together by chlorine bridges forming pairs of polymeric ···Cu–Cl–Cu···Cl···Cu zigzag chains parallel to the b axis. The copper atoms are coordinated by four nitrogen atoms of the macrocyclic ligand (average Cu–N = 2.04 (1) Å) and one chloride ion (Cu–Cl = 2.48 (2) Å), forming a distorted square pyramid. One further chloride ion at 3.31 (2) Å completes a distorted elongated octahedron. The electrochemical behavior of the dinuclear complex $[Cu_2(bistrien)]^{4+}$ was investigated in aqueous solution by cyclic voltammetry. The complex undergoes a two-electron reversible reduction into the dinuclear Cu(I) species, by two independent monoelectronic steps. The reduced species is unstable with respect to the demetalation and reduction to metal.

Introduction

The coordination chemistry of the macrocyclic metal complexes has widely grown in recent years.[2] Among polyazamacrocycles the tetraazacycloalkanes are by far the most studied. Many papers have been published dealing with tetraaza macrocycles.[3–5] Much less is instead known about the thermodynamics protonation and metal complex formation of large polyazacycloalkanes (more than six nitrogens as donor atoms), for which only few publications have appeared in literature until now.[6,7] The possibility for these

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