Inorg. Chem. **1990**, *29*, 4805–4808

authors do not report the properties of the frozen-solution spectrum for this complex.[22]

Visible Spectra. $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ has a charge-transfer band in the visible spectrum at 530 nm with an ϵ value of 1000 M^{-1} cm^{-1}. When the Mo(VI) complex is reduced with one electron to the green Mo(V) monomer, two bands are observed in the visible spectrum, one at 610 nm with an ϵ value of 2300 M^{-1} cm^{-1} and a second band at 400 nm with an ϵ value of 15 000 M^{-1} cm^{-1}. The Mo(V) monomer can be reduced with one electron to a brown Mo(IV) complex that has a band at 445 nm (ϵ = 10 000 M^{-1} cm^{-1}) in the visible spectrum.

Conclusions. The new complex, $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$, is the first example of a molybdenum(VI) complex with a chelating imido ligand. The geometry of the complex is distorted pentagonal bipyramidal. The molybdenum nucleus in this complex, as observed by ^{95}Mo NMR spectroscopy, is deshielded by about 500 ppm; the imido nitrogen, observed by ^{14}N NMR spectroscopy, is deshielded by about 90 ppm compared to that of other seven-coordinate Mo(VI) imido complexes. In contrast to other seven-coordinate Mo(VI) imido compounds, the complex can be reduced with one electron to yield a Mo(V) monomer. The Mo(V) complex can be reversibly reduced with a second electron to a Mo(IV) species. We are currently working on the synthesis of related complexes with different Mo(VI) starting materials to see if a complex with a reversible two-electron redox pathway, as found for molybdenum in hydroxylases, can be isolated.

Acknowledgment. We thank the William and Flora Hewlett Foundation of the Research Corp. for partial support of this research. M.M. thanks Grinnell College for a Harris Fellowship and Prof. J. T. Spence at Utah State Univesity for helpful discussions and the use of his laboratory for electrochemical and EPR experiments.

Supplementary Material Available: Tables listing the complete structure determination summary, atomic coordinates and equivalent isotropic and anisotropic displacement coefficients for all atoms including H atoms, bond lengths, and bond angles (8 pages); a table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Steric Control of Tricoordination in Univalent Coinage Metal Complexes: Crystal Structure of Tris(cyclopentyldiphenylphosphine)silver(I) Tetrafluoroborate

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Eighteen complexes of general formula $[M(PR_2R')_3]X$ (M = Cu, Ag, Au; X = BF_4, ClO_4; R = Ph, Cy, C_5H_9) have been isolated and characterized. In the majority of cases, the infrared spectra of the anions indicate that they are not coordinated or, at most, very weakly coordinated. Thus three-coordination is indicated. This intermediate coordination number for univalent coinage metals is produced by steric limitations of the tertiary phosphine ligands. The PR_2R' ligands employed are intermediate in size between tricyclohexylphosphine, which forms two-coordinate complexes, and triphenylphosphine, which forms four-coordinate complexes. Crystals of $[Ag\{PPh_2(C_5H_9)\}_3][BF_4]$ belong to the trigonal space group $P\bar{3}1c$, with a = 13.398 (6) Å, c = 30.509 (10) Å, and Z = 4. The structure refinement converged at R = 0.0551. The structure consists of nonplanar three-coordinate Ag–phosphine complexes and disordered BF_4^- anions. The silver ions are located on sites of 3-fold symmetry (Ag–P = 2.545 (3) Å, P–Ag–P = 117.4 (1)°). The $Ag(PR_2R')_3$ cations are found in pairs about a single disordered BF_4^- anion. Weak Ag–BF_4 interactions (Ag···F = 2.54 (2) Å) induce the deformation of the AgP_3 core from planarity.

Introduction

It has been the aim of the research investigations in one of our laboratories to study the role of size and ligation properties of tertiary phosphines (as well as tertiary arsines) upon the stereochemistry of cationic, univalent coinage metal complexes. Prior to this work the only unambiguously characterized, three-coordinate complexes containing three group VB ligands were the $[Au(PPh_3)_3]X$ (X = BPh_4, $B_9H_{12}S$) complexes.[1,2] Triphenylphosphine, despite its cone angle of 145°,[3] forms four-coordinate $[M(PPh_3)_4]^+$ (M = Cu, Ag) cations,[4] but it has been shown recently that larger tertiary phosphine or arsine ligands form two-coordinate complexes with univalent coinage metals.[5] These complexes are frequently distorted from linear coordination because of weak interactions between the anions and the cations. Thus they are effectively precursors of three-coordinate acido complexes. It was believed that if somewhat smaller ligands of this type were to be employed, it should then be possible to prepare three-coordinate, cationic complexes. Construction of molecular models suggested that cycloalkyldiphenylphosphines would be able to form the desired $[M(PRPh_2)_3]^+$ cations. Indeed, that has been observed, and in this paper, we present the results on the new complexes prepared of this type, as well as the structure of one specific compound, $[Ag\{PPh_2(C_5H_9)\}_3]BF_4$.

Table I. Physical Properties of Complexes Containing Three Tertiary Alkylphosphine Ligands

complex	conductivity[a]/S	anion peaks[b]/cm^{-1}	anion symmetry
$[Cu\{PPh(C_5H_9)_2\}_3][ClO_4]$	26.7	1100, 625	T_d
$[Cu(PPhCy_2)_3][BF_4]$	29.4	1050	T_d
$[Cu(BF_4)(PPh_2Cy)_3]$	25.7	1085, 980	C_{3v}
$[Cu(ClO_4)(PPh_2Cy)_3]$	25.5	1115, 1050, 625	C_{3v}
$[Cu\{P(C_5H_9)Ph_2\}_3][BF_4]$	27.6	1050	T_d
$[Cu\{P(C_5H_9)Ph_2\}_3][ClO_4]$	26.7	1090, 620	T_d
$[Cu(BF_4)\{P(C_7H_{13})Ph_2\}_3]$	23.8	1080, 975	C_{3v}
$[Cu\{P(C_7H_{13})Ph_2\}_3][ClO_4]$	25.6	1100, 615	T_d
$[Ag(PCy_2Ph)_3][BF_4]$	26.6	1050	T_d
$[Ag(PCy_2Ph)_3][ClO_4]$	26.6	1085, 620	T_d
$[Ag(PCyPh_2)_3][BF_4]$	24.7	1050	T_d
$[Ag(PCyPh_2)_3][ClO_4]$	26.3	1090	T_d
$[Ag\{P(C_5H_9)Ph_2\}_3][BF_4]$	26.0	1055	T_d
$[Ag\{P(C_7H_{13})Ph_2\}_3][BF_4]$	27.0	1050	T_d
$[Ag\{P(C_7H_{13})Ph_2\}_3][ClO_4]$	26.7	1095, 620	T_d
$[Ag\{P(C_5H_9)Ph_2\}_3][ClO_4]$	26.8	1090, 1070, 620	T_d
$[Au\{PPh_2(C_5H_9)\}_3][ClO_4]$		1090	T_d
$[Au\{PPh_2(Cy)\}_3][ClO_4]$		1100	T_d

[a] Determined on all nitrobenzene solutions. [b] Nujol mull spectra.

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[‡] Washington State University.

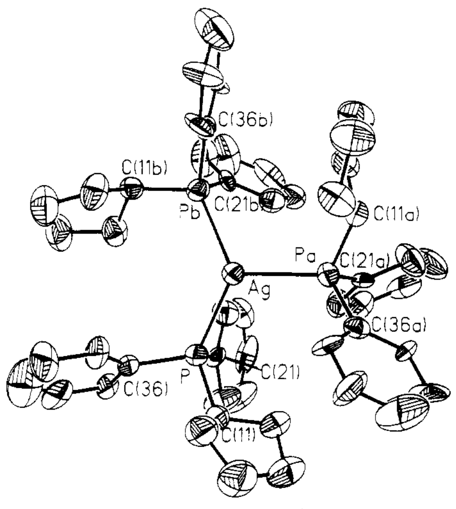

Figure 1. Illustration of $[Ag\{PPh_2(C_5H_9)\}_3]^+$ cation.

Discussion

A total of 14 copper(I), silver(I), and gold(I) complexes were synthesized from diphenylcycloalkyl phosphines. Two copper(I) and two silver(I) $(ML_3)X$ salts were isolated containing dicycloalkylphenylphosphines. The pertinent physical properties of these are tabulated in Table I. In most cases, the spectroscopic and conductivity data are consistent with their formulation as simple $[ML_3]^+$ cationic species. There is some evidence from the physical properties of the complexes that significant interaction between copper(I) cations and the anions occurs in three of the compounds (entries 3, 4, and 7, Table I). In the limit, this would give rise to acido complexes corresponding to $[Cu(FBF_3)(PPh_3)_3]$,[6] but the lifting of degeneracy in the infrared spectra of these complexes may merely arise from site symmetry distortion of the anions from pure T_d symmetry. No acido silver(I) complexes were encountered. Conversely, the absence of splitting of the ν_4 band is not definitive proof of the lack of weak cation–anion interactions. Hence the structure determination of one salt, $[Ag\{PPh_2(C_5H_9)\}_3]BF_4$, where no interaction between cation and anion was indicated, was undertaken.

The crystal structure of $[Ag\{PPh_2(C_5H_9)\}_3]BF_4$ is trigonal, with the $Ag\{PPh_2(C_5H_9)\}_3^+$ cations located on sites with 3-fold symmetry (Figure 1). Pairs of these cations are sandwiched about a disordered BF_4^- anion at $(^2/_3, {}^1/_3, {}^1/_4)$. The disorder is such that each Ag ion has a 50% probability of forming an electrostatic bond of length 2.54 (2) Å with a fluorine atom (F(1)) lying on the 3-fold axis. The other BF_4^- anion, occupying an interstial site, is also disordered. The $Ag-BF_4$ interaction causes a slight distortion from planarity of the AgP_3 core of the cationic complex. The Ag–P bonds (Ag–P = 2.545 (3) Å) are bent back away from the anion, with a P–Ag–F (1) angle of 99.4 (1)°, with a subsequent diminution of the P–Ag–P angle from 120 to 117.4 (1)°. The Ag ion lies 0.415 Å out of the plane of the three phosphorus atoms.

The organic rings are deployed about each phosphorus atom such that two (one phenyl, one cyclopentyl) lie roughly in the equatorial plane, partially encapsulating the BF_4^- anion. The third ring, a phenyl group, protrudes above the equatorial plane. The ability to form this $AgL_3^+-BF_4^--AgL_3^+$ species is likely quite stereospecific and should depend quite critically on the steric factors associated with the three R groups.

The geometry of this Ag complex is intermediate between that expected for the hypothetical free complex (containing a planar AgP_3 core) and that observed in $Cu(BF_4)(PPh_3)_3$. In the latter, the BF_4^- anion is, in the words of the authors,[6] "weakly coordinated" to the copper(I) ion and leads to a pronounced distortion from planarity (P–Cu–F = 102.2°, P–Cu–P = 115.6°). It is interesting to note that, in both cases, the M–F distance is essentially the same as the M–P distance (Ag–F = 2.54 Å, Ag–P = 2.542 Å; Cu–F = 2.31 Å, Cu–P = 2.298 Å). However, the presence of disorder in the Ag salt leads to a net interaction that is somewhat weaker.

Previously,[5] we have demonstrated that the σ-bond radius of three-coordinate silver(I) is 1.49 Å. If the internally consistent σ-bond radius of phosphorus, 1.13 Å (obtained by subtracting 0.70 Å from the mean P–sp^2-C distance of 1.83 Å), is added to this, then, for a purely σ-bond, the Ag–P distance should be 2.62 Å. The observed shortening of some 4%, as in the case of $[Ag\{PPh_2(C_5H_9)\}_2]^+$,[5] is indicative of some $d\pi$–$d\pi$ interaction between silver and phosphorus. That the silver(I)–phosphorus bond length is 0.1 Å greater in the three-coordinate complex is only to be expected since both the coordination of an additional π-acid ligand and the increase in covalent radius with coordination number will lengthen the bond.

No copper(I) or silver(I) cations containing four tertiary phosphine ligands were obtained even at ligand:metal ratios in the preparative reactions of 6:1. Hence, it would appear that PPh_3 is the largest tertiary phosphine capable of forming $[ML_4]^+$ species. Indeed this only holds true for the perchlorate[7] salts since the acido complex $[Cu(BF_4)(PPh_3)_3]$[6] has been fully characterized. In the latter complex the inclusion of the acido ligand so reduces the interligand repulsion energies that the formation of only three strong Cu–P bonds together with a weak $Cu-FBF_3$ bond is more favorable than forming four Cu–P bonds.

The PPh_2(cycloalkyl) ligands normally form $[ML_3]X$ complexes, and $[ML_2]X$ complexes are formed only exceptionally at low ligand:metal ratios during their preparation formed. No $[MXL_3]$ complexes (cf. $[Cu(BF_4)(PPh_3)_3]$ above) were isolated in this work, and it can be assumed that PPh_2R ligands effectively fill the coordination spheres of the univalent coinage metals and leave no room for the coordination of the small, tetrahedral anions of low coordinating powder. Indeed, the PPh_2R ligands seem to be at the size limit for three-coordination since, unlike some of the $PPh(cycloalkyl)_2$ series of ligands, they do not exclusively form $[ML_3]X$ complexes. The latter series of ligands form only $[ML_3]X$ complexes at high ligand:metal ratios, but at lower ratios, $[ML_2]X$ complexes are always obtained.[5] The absence of clear steric limits for the formation of two- or three-coordinate cations arises from the meshing capabilities of the ligands' organo groups.[8]

Experimental Section

Ligands were synthesized from $PPhCl_2$ and PPh_2Cl as previously described.[5] Copper and silver complexes were prepared from the appropriate hydrated copper(II) or anhydrous silver(I) salts, respectively, by allowing them to react with a minimum of 3.5 equiv of ligands in ethanolic solution. The methods of isolation and purification of these compounds have been described earlier.[5] The preparation of gold(I) complexes followed the methods given earlier, but care was taken to ensure that more than the stoichiometric quantity of ligand was employed.[5]

Carbon and hydrogen microanalyses were carried out by Mr. M. F. Newman of the North East London Polytechnic Analytical Service. Phosphorus and arsenic microanalyses were carried out by Analytische Laboratorien, Elbach, Gummersbach, Federal Republic of Germany. Conductivity measurements were made on millimolar nitrobenzene solutions, thermostated at 25 °C, using a Wayne Kerr Universal Bridge B221. The cell constant was determined by using aqueous potassium chloride solutions of known concentration. AR grade nitrobenzene was further purified by drying it over $CaCl_2$ and redistilling; the fraction distilling in the range 209–211 °C (760 mmHg) was collected and used immediately. Melting points were determined in an Electrothermal melting point apparatus and are uncorrected. Infrared spectra were obtained in "Nujol" or hexachlorobuta-1,3-diene mulls between potas-

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Table II. Melting Points and Analytical Data for $[ML_3]X$ Complexes Prepared

		anal.					
		found			calcd		
compd	mp/°C	% C	% H	% Z	% C	% H	% Z
$[Cu\{PPh(C_5H_9)_2\}_3][ClO_4]$	119–123	63.55	7.50	10.18	63.91	7.70	10.30
$[Cu(PPhCy_2)_3][BF_4]$	189–212	66.30	8.17		66.62	8.38	
$[Cu(BF_4)(PPh_2Cy)_3]$	192–194	67.91	7.00		67.89	6.65	
$[Cu(ClO_4)(PPh_2Cy)_3]$	165–166	67.00	6.86	9.27	67.00	6.56	9.59
$[Cu\{PPh_2(C_5H_9)\}_3][BF_4]$	171–173	67.06	6.52	10.11	67.07	6.29	10.29
$[Cu\{PPh_2(C_5H_9)\}_3][ClO_4]$	139–141	65.89	6.07	10.26	66.16	6.20	10.03
$[Cu(BF_4)(PPh_2(C_7H_{13})\}_3]$	197–198	68.50	7.32		68.64	6.97	
$[Cu(PPh_2(C_7H_{13})\}_3][ClO_4]$	197–199	68.03	6.60	8.93	67.78	6.89	9.20
$[Ag(PPhCy_2)_3][BF_4]$	205–207	63.83	8.49		63.72	8.04	
$[Ag(PPhCy_2)_3][ClO_4]$	190–212	62.90	8.25	9.07	62.94	7.92	9.01
$[Ag(PPh_2Cy)_3][BF_4]$	186–188	64.82	6.78		64.87	6.30	
$[Ag(PPh_2Cy)_3][ClO_4]$	183–185	64.07	6.46	9.35	64.06	6.27	9.18
$[Ag(PPh_2(C_5H_9)\}_3][BF_4]$	144–145	64.18	6.02	9.60	63.96	5.99	8.70
$[Ag(PPh_2(C_7H_{13})\}_3][BF_4]$	197–198	65.59	7.25	9.60	65.71	6.67	9.70
$[Ag(PPh_2(C_7H_{13})\}_3][ClO_4]$	149–150	65.22	6.63	9.00	64.93	6.59	8.74
$[Ag(PPh_2(C_5H_9))_3]ClO_4$	137–138	63.50	6.17		63.13	6.17	
$[Au(PPh_2(C_5H_9))_3][ClO_4]$	117–122	58.30	5.42	8.02	57.82	5.40	8.77
$[Au(PPh_2Cy)_3][ClO_4]$	160–161	58.55	6.08	8.29	58.88	5.76	8.40

Table III. Crystal Parameters for $\{Ag[P(C_5H_9)(C_6H_5)_2]_3\}BF_4$

formula	$C_{51}H_{57}AgBF_4P_3$
cryst class	trigonal
a/Å	13.398 (6)
c/Å	30.509 (10)
V/Å^3	4742.7
T/°C	22
space group	$P\bar{3}1c$
radiation (λ/Å)	Mo Kα (0.71069)
μ/cm^{-1}	3.61
ρ/g cm^{-3}	1.37 (Z = 4)
R	0.055
R_w	0.057

sium bromide plates on either a Perkin-Elmer 377 or a Perkin-Elmer 781 spectrophotometer, the latter in conjunction with a Perkin-Elmer 3600 data station.

The crystal structure of the colorless hexagonal prismatic shaped crystals of $[Ag\{PPh_2(C_5H_9)\}_3][BF_4]$ was determined by using diffraction data collected on a Nicolet R3m/E diffractometer system utilizing Mo Kα radiation (λ = 0.71069 Å).[9] Systematic absences indicated $P31c$ and $P\bar{3}1c$ as the possible space group choices for the trigonal crystal. Intensity statistics indicated the presence of a center of inversion, which was confirmed by the successful solution and refinement in the latter space group. In addition, the choice of the acentric space group would have required the existence of two independent $[Ag\{PPh(C_5H_9)\}_3]^+$ cations per asymmetric unit. The structure was solved via the direct-methods program SOLV in the SHELXTL structure solution package.[10] This yielded heavy-atom (Ag, P) positions, and lighter atoms were located on subsequent difference syntheses. A summary of crystal data and refinement results are given in Table III. Final positional parameters are given in Table IV, and pertinent bond distances and angles are reported in Table V. A full summary of data collection and refinement parameters are included in the supplementary material, as well as a complete listing of bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions.

The structure refinement for the tris(cyclopentyldiphenylphosphine)silver(I) complex cation portion of the structure was straightforward. However, both crystallographically inequivalent BF_4^- anions were disordered. One BF_4^- anion (B, F(1), F(2)) is located halfway between two cations at a site of D_3 symmetry. The 2-fold disorder for this anion is adequately described by the reported position with F(1) lying on the 3-fold axis and three symmetry related F(2) atoms completing the base of one tetrahedron. The second orientation is generated by the mirror plane perpendicular to the 3-fold axis. The situation is not clear for the second site. This anion (B(11), F(11), F(12)) is situated at a site of S_6 symmetry with the boron atom nominally located at the origin. However, the fluorine positions would indicate that the disorder involves a displacement of the center of the anion from the origin. Because of the small scattering power of the boron atom and the lack of interaction of this anion with the phosphine complex of interest, a more detailed de-

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

atom	x	y	z	U[a]
Ag	6667	3333	1283 (1)	39 (1)
P	8165 (2)	2731 (2)	1147 (1)	41 (1)
C(11)	9661 (6)	3763 (6)	1294 (2)	42 (4)
C(12)	10131 (7)	4968 (6)	1095 (3)	59 (5)
C(13)	11183 (7)	5756 (7)	1375 (3)	86 (6)
C(14)	11035 (9)	5129 (9)	1805 (3)	96 (7)
C(15)	9875 (7)	4024 (7)	1777 (3)	72 (5)
C(22)[b]	7236 (4)	2223 (4)	314 (2)	52 (5)
C(23)	7244	2110	−140	65 (6)
C(24)	8245	2295	−352	72 (6)
C(25)	9238	2592	−109	95 (6)
C(26)	9230	2705	345	78 (6)
C(21)	8229	2521	557	38 (3)
C(31)[b]	8293 (4)	685 (4)	1167 (2)	52 (4)
C(32)	8196	−289	1373	83 (5)
C(33)	7812	−538	1805	105 (7)
C(34)	7524	188	2032	107 (5)
C(35)	7621	1162	1826	68 (4)
C(36)	8006	1411	1393	44 (3)
F(2)	7660 (14)	3596 (23)	2360 (9)	242 (24)
B	6667	3333	2500	56 (7)
B(11)	0	0	0	92 (12)
F(1)	6667	3333	2115 (7)	202 (23)
F(11)	−43 (76)	−444 (34)	308 (11)	80 (15)
F(12)	247 (40)	959 (17)	261 (7)	251 (23)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Phenyl rings constrained as rigid bodies.

Table V. Interatomic Lengths (Å) and Angles (deg)

	Lengths		
Ag–P	2.545 (3)	C(11)–C(12)	1.534 (11)
Ag–F(1)	2.539 (22)	C(12)–C(13)	1.531 (10)
P–C(11)	1.832 (6)	C(14)–C(15)	1.521 (10)
P–C(21)	1.831 (7)	B–F(1)	1.173 (22)
P–C(36)	1.833 (6)	B–F(2)	1.267 (21)
C(11)–C(15)	1.511 (10)	B(11)–F(11)	1.097 (41)
C(13)–C(14)	1.517 (14)	B(11)–F(12)	1.402 (25)
	Angles		
P–Ag–F(1)	99.4 (1)	P–C(21)–C(22)	117.1 (2)
P–C(11)–C(12)	114.6 (6)	P–C(21)–C(26)	122.8 (2)
P–Ag–P[a]	117.4 (1)	P–C(36)–C(35)	117.9 (2)
P–C(11)–C(15)	115.0 (5)	P–C(36)–C(31)	122.0 (2)
Ag–P–C(11)	117.4 (3)	C(11)–P–C(21)	103.8 (3)
Ag–P–C(21)	108.3 (2)	C(11)–P–C(36)	100.6 (3)
Ag–P–C(36)	120.6 (2)		

[a] Denotes atom related by the symmetry operation $\bar{y}, x - y, z$.

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scription of the disorder was not pursued.

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Supplementary Material Available: Tables of crystal data, hydrogen atom positions, and thermal parameters (4 pages); a table of F_o/F_c data (7 pages). Ordering information is given on any current masthead page.

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Organic Substituent Effects in Macrobicyclic (Hexaamine)cobalt(III/II) Complexes: A New Method of Obtaining Polar Substituent Constants

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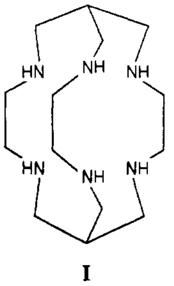
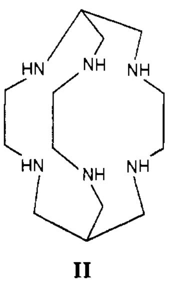
The redox potentials, $E_{1/2}$, for the reversible cobalt(III/II) redox couples of complexes of substituted macrobicyclic ligands derived from 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane show a substantial variation with the type of substituent. The variation was subjected to a Hammett type treatment yielding a series of inductive or polar substituent constants σ_E that correlate with the organic substituent constants (σ_I) obtained by a variety of other methods. Changes in $E_{1/2}$ with substituent are not reflected in changes in the ligand field spectra of either oxidation states. We deduce, therefore, that the effects are not transmitted via through-space overlap of orbitals or through-bond induction. The effects can be attributed to either a through-space Coulombic mechanism or interactions through the σ framework. In the case of the NHR_2^+ and NR_3^+ substituents, there is a steric substituent effect that forces the Co(III) cage complexes from a lel_3 to ob_3 conformation and results in quite different spectroscopic and electrochemical properties. The correlations of σ_E values with the ^{1}H, ^{13}C, and ^{59}Co NMR chemical shifts are also examined. The σ_E constants are readily obtained, and this may prove to be a more versatile method of obtaining polar substituent constants than those currently used in physical organic chemistry.

Introduction

Macrobicyclic (hexaamine)cobalt(III) complexes of ligands with the parent structures 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane (sar, I) and 3,6,10,13,15,18-hexaazabicyclo[6.6.5]nonadecane (absar, II) invariably show chemically reversible Co(III)/Co(II) redox couples.[1] An irreversible reduction of the substitutionally inert Co(II) complexes occurs also at appreciably more negative potentials,[1] but there is no sign that the Co(IV) state is accessible. The Co(III)/Co(II) redox couple is affected by ligand cavity size, by ligand conformation, and by the type of substituents on the parent macrobicycles (or "cage" ligands). A physical model for describing these effects has been developed.[2] Generally, the first metal-centered reduction precedes any functional group reduction processes, and hence, substitution-inert cobalt(III) and cobalt(II) complexes with a wide variety of substituents become accessible.

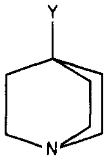


I

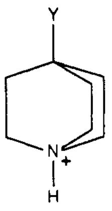


II

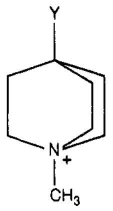
In this paper, the variation of redox potential with substituent is subjected to a Hammett type treatment[3] and correlations with ^{1}H, ^{13}C, and ^{59}Co NMR spectra are made. Similarities between the apically substituted encapsulated cobalt complexes and quinuclidines (III) and quinuclidium salts (IV, V) are evident, particularly when the disposition of the cobalt ion relative to the substituents on the cage cap (VI) is considered. In general, the large amount of data obtained for the effects of substituents on the physical properties of these related bicyclic organic systems, by Grob and co-workers,[4-6] allows useful comparisons to be made. Previously, correlations between the ligand field parameter (Δ) and $E_{1/2}$ for reduction at the metal center have been reported.[7,8]



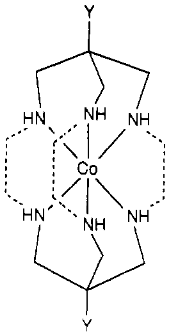
III



IV



V



VI

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