3822 *Inorg. Chem.* **1984**, *23*, 3822-3825

is clear that the order of activation energies is Zn^{2+} $\simeq$ Mn^{2+} $\gg$ Ca^{2+}.[21] This is in reasonable agreement with the theory, particularly when it is realized that the activation entropies should be large positive for Zn^{2+}, small for Mn^{2+}, and large negative for Ca^{2+}. In terms of dielectric continuum theory, i.e. Born theory or modifications thereof, one would expect differences in ΔH_s(ts) and ΔH_s(oct) to be small although size differences between transition state and octahedral ground state might imply that any lowering of activation energy would be larger for Zn^{2+} than for Ca^{2+}.

Recent molecular-dynamics calculations have led to a much greater understanding of the detailed structural and dynamic aspects of water molecules in the vicinity of an ion. However, in order to solve the equations of motion accurately, it is necessary to use a very short time step (2×10^{-16} s) and this clearly limits the total time scale to a few picoseconds, much shorter than the time scale of solvent exchange. In order to study such chemical processes, it is necessary to equilibrate the system with the ion and its near neighbors fixed close to a plausible transition-state structure and then to study the return to equilibrium once the constraints are removed. This has yet to be done for aqueous electrolyte solutions.

The recent work of Heinzinger and co-workers on Mg^{2+} [22-24] clearly shows that the number of water molecules in the first hydration shell is exactly six and during the 3.3 ps of the simulation there was no exchange as expected. Their estimates of the simultaneous occupancy of octahedral sites and of various angular correlations clearly indicate octahedral coordination although it is apparently easily distorted. This agrees with our results that energies are relatively insensitive to small distortions and is also borne out by the very low-frequency Raman lines for the symmetric stretching vibration of aquated cations.[25] More significant to this work is the existence of a well-defined second shell containing 15 or so molecules that are still preferentially oriented with respect to the ion. It is clear that this second solvation shell will affect the energies of both the transition state and the ground state. The failure of our approach to give a reasonable transition-state structure for Zn^{2+} with the angle θ unconstrained is almost certainly due to neglect of second-shell effects, which can stabilize the exchanging water molecules that are well removed from the ion.

Acknowledgment. We acknowledge the Natural Sciences and Engineering Research Council of Canada for support for this work.

Registry No. H_2O, 7732-18-5; $Cu(H_2O)_6^{2+}$, 17787-72-3; $Mn(H_2O)_6^{2+}$, 15365-82-9; $Zn(H_2O)_6^{2+}$, 15906-01-1.

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Notes

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Preparation and Properties of New Pentacoordinate Iron Nitrosyl Complexes

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Our interest in the chemistry of the nitrosyl complexes has been mainly devoted to the use of monodentate phosphite as coligand, and in this context, the syntheses of pentacoordinate $\{Co(NO)\}^8$ complexes[1] of the type $[CoXL_3(NO)]^+$ and $[CoL_4(NO)]^{2+}$ have recently been reported.[2] Similar investigations carried out on iron(II) halides by using gaseous NO allowed us to obtain new pentacoordinate $[FeL_4(NO)]^+$ (L = phosphite) derivatives, which are described in the present report. Furthermore, whereas some iron nitrosyl compounds also containing CO have been described,[3] no example of isocyanide–phosphine derivatives known to us has yet been reported. Therefore, in this paper we also present the reactivity of the $[FeL_4(NO)]^+$ species with isocyanides, leading to the synthesis of the first nitrosyl isocyanides–phosphite mixed-ligand complexes.

Results and Discussion

Nitric oxide reacts at room temperature with FeX_2 (X = Cl, Br) solutions containing an excess of phosphite to give the pentacoordinate nitrosyl $[FeL_4(NO)]^+$ (L = $P(OMe)_3$, $P(OEt)_3$) complexes.[4]

If the reaction is carried out employing a bulky ligand such as $PPh(OEt)_2$ or $P(O\text{-}i\text{-}Pr)_3$, only intractable oils are obtained, whose infrared spectra do not show in the NO stretching region bands attributable to the $[FeL_4(NO)]^+$ species. Therefore, only with phosphites of little steric hindrance does the reaction proceed, to give the $\{Fe(NO)\}^8$ complexes that were isolated and characterized.[5]

Selected properties of the new $[FeL_4(NO)]^+$ compounds are reported in Table I. They are stable both in the solid state

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[1] The nitrosyl complexes have been classified according to the $\{M(NO)\}^n$ nomenclature: Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339; *Top Stereochem.* **1981**, *12*, 155.

[2] (a) Albertin, G.; Bordignon, E.; Canovese, L.; Orio, A. *Inorg. Chim. Acta* **1980**, *38*, 77. (b) Albertin, G.; Bordignon, E.; Mazzocchin, G.; Orio, A.; Seeber, R. *J. Chem. Soc., Dalton Trans.* **1981**, 2127. (c) Albertin, G.; Pelizzi, G.; Bordignon, E. *Inorg. Chem.* **1983**, *22*, 515 and references therein.

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[4] From the reaction of FeX_2 with phosphites, we were able to isolate only the $[FeBrL_5]^+$ cation, which quickly reacted with NO to give the dinitrosyl $[FeL_2(NO)_2]$ as the main product. Only a small amount of $[FeL_4(NO)]^+$ was observed. The $[FeL_2(NO)_2]$ complex has been prepared by an alternative procedure: Kruck, T.; Waldmann, J.; Hoefler, M.; Birkenhaeger, G.; Odenbrett, C. *Z. Anorg. Allg. Chem.* **1973**, *402*, 16.

[5] (a) The previously reported complexes $[FeL_2(NO)]^+$ (L = 1,2-bis(diphenylphosphino)ethane) and $[FeL(NO)]^+$ (L = (2,2,2-tris(diphenylphosphino)ethyl)amine) have been obtained with bi- or tetradentate phosphine ligands. See ref 3a. (b) Hoffman, P. R.; Miller, J. S.; Ungermann, C. B.; Caulton, K. J. *J. Am. Chem. Soc.* **1973**, *95*, 7902. (c) Di Vaira, M.; Ghilardi, C. A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 1555.

0020-1669/84/1323-3822$01.50/0

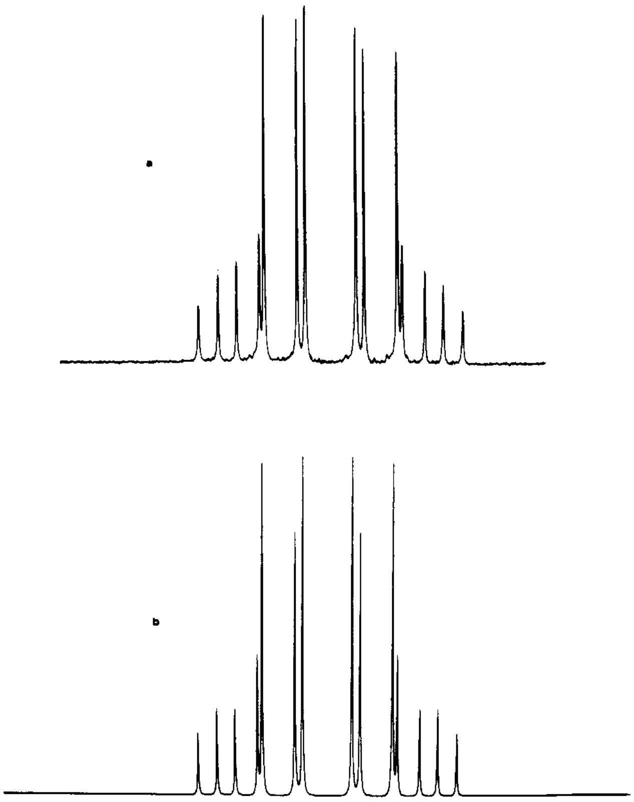
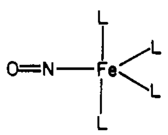


Figure 1. Observed (a) and calculated (b) ${}^{31}P\{^1H\}$ NMR spectra at −60 °C for a $(CD_3)_2CO$ solution of $\{Fe[P(OEt)_3]_4(NO)\}BPh_4$. The simulated spectrum was obtained with an A_2B_2 model and the NMR parameters given in the text.

and in solution of polar organic solvents and diamagnetic, and conductivity values (53.6–58.0 Ω^{-1} M^{-1} cm^2 in nitromethane solutions) are in agreement with those reported for 1:1 electrolytes containing BPh_4 as anion.[6]

The infrared spectra in the NO stretching region show only one strong band at 1734 cm^{-1} ($P(OEt)_3$) or 1747 cm^{-1} ($P(OMe)_3$) in dichloromethane solution and at 1722 cm^{-1} in the solid state, suggesting the presence of a linear MNO group.[7]

The ${}^{31}P\{^1H\}$NMR spectra of the $[FeL_4(NO)]^+$ complexes at room temperature consist of a singlet at δ +154.5 ($P(OEt)_3$) or δ +156.7 ($P(OMe)_3$). Lowering the sample temperature produces a complex sequence of changes in the ${}^{31}P$ spectra until, at −60 °C in acetone-d_6, the pattern shown in Figure 1a is observed. Computer simulation for an A_2B_2 model using NMR parameters $(J(P_AP_B)) = 138.6$ Hz and $(\delta(P_AP_B)) = 374.5$ Hz is also reported in Figure 1b.[8] The good fit obtained between the observed and calculated spectra[9] suggests a trigonal-bipyramidal structure for the cation (I) with the NO



I

group in the equatorial position. The addition of free phosphite to the solution of the complex does not change the profile of the spectra in the temperature range −70 to +40 °C, and the

Table I. Selected IR, NMR, and Electronic Absorption Data for the Iron Nitrosyl Complexes

compd	$\nu(NO)$,[a] cm^{-1}	$\nu(CN)$,[a] cm^{-1}				λ_{max}, nm $(10^{-3}\epsilon)$[b]		¹H chem shift,[c,d] τ			${}^{31}P\{^1H\}$ chem shift,[c-e] δ
								CH_2 phosphite	CH_3 iso-cyanide	CH_3 phosphite	
$\{Fe[P(OEt)_3]_4(NO)\}BPh_4$	1734 s (1722 s)					320 (0.81)	463 (0.11)	5.88 m		8.69 t	+154.5
$\{Fe[P(OMe)_3]_4(NO)\}BPh_4$	1747 s (1722 s)					316 (0.90)	442 (0.13)			6.30 m	+156.7
$\{Fe[P(OEt)_3]_2(4\text{-}CH_3C_6H_4NC)_2(NO)\}BPh_4$	1756 s (1750 s)	2140 s (2140 s)	2096 s (2095 s)	2038 vw (2040 vw)		320 (15.9)	451 (1.3)	5.67 m	7.63 s	8.61 t	+156.9
$\{Fe[P(OEt)_3]_2(4\text{-}CH_3OC_6H_4NC)_2(NO)\}BPh_4$	1754 s (1748 s)	2135 s (2140 s)	2095 s (2100 s)	2038 vw (2041 vw)		312 (21.6)	462 (1.2)	5.69 m	6.19 s	8.62 t	+153.6
$\{Fe[P(OEt)_3]_2[2,6\text{-}(CH_3)_2C_6H_3NC]_2(NO)\}BPh_4$	1750 s (1747 s)	2152 sh (2158 sh)	2134 s (2140 s)	2090 s (2095 s)	2000 vw	308 (6.8)	444 (1.4)	5.69 m	7.53 s	8.68 t	+155.7
$\{Fe[P(OEt)_3]_2(4\text{-}NO_2C_6H_4NC)_2(NO)\}BPh_4$	1767 s (1763 s)	2131 s (2132 s)	2080 s (2080 s)	2066 s (2065 s)	2006 vw	306 (20.6)	370 (19.4) 430 sh	5.57 m		8.56 t	+153.2
$\{Fe[P(OEt)_3]_2(C_6H_5NC)_2(NO)\}BPh_4$	1756 s (1770 s)	2137 s (2138 s)	2090 s (2088 s)	2000 vw (2000 vw)		322 (14.0)	456 (1.2)	5.69 m		8.62 t	+156.3
$\{Fe[P(OMe)_3]_2(4\text{-}CH_3C_6H_4NC)_2(NO)\}BPh_4$	1762 s (1755 s)	2141 s (2140 s)	2098 s (2095 s)	2037 vw (2040 vw)		318 (17.5)	460 (1.1)		7.64 s	6.08 t	+163.2

[a] Frequencies in parentheses are from spectra of KBr pellets of complexes in the solid state; all other values are from spectra of CH_2Cl_2 solutions. [b] In CH_2Cl_2 solutions. [c] In $(CD_3)_2CO$. [d] At room temperature. [e] Positive shift downfield from 85% H_3PO_4.

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(8) An A_2B_2 pattern with $(J(P_AP_B)) = 139.0$ Hz and $(\delta(P_AP_B)) = 410.9$ Hz is also observed at −70 °C in CD_2Cl_2. The subsequent addition of acetone does not change the profile of the spectrum.

(9) For the $\{Fe[P(OMe)_3]_4(NO)\}BPh_4$ complex an A_2B_2 spectrum with $(J(P_AP_B)) = 140.6$ Hz and $(\delta(P_AP_B)) = 339.8$ Hz is observed at −60 °C in $(CD_3)_2CO$.

peak of excess $P(OEt)_3$ or $P(OMe)_3$ remains sharp throughout, confirming that the exchange observed is intramolecular. For five-coordinate d^8 phosphite complexes,[10] phosphorus exchange occurs through an intramolecular rearrangement following the Berry pseudorotation process;[11] this likely applies to the present exchange.

The new pentacoordinate $[FeL_4(NO)]^+$ complexes are relatively stable to the substitution of either the nitrosyl or the phosphite ligands. No reaction is observed with CO (1 atm), with halogenide ions (Cl^-, Br^-, I^-), or with phosphite in refluxing ethanol or methanol. Treatment with nitric oxide results in some decomposition, but no new nitrosyl species is detected.

In contrast, the $[FeL_4(NO)]^+$ cations react with aryl isocyanides to give the mixed-ligand complexes $[FeL_2(CNR)_2(NO)]^+$ (R = C_6H_5, $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$, $4\text{-}NO_2C_6H_4$, $2,6\text{-}(CH_3)_2C_6H_3$) as shown in

$$[FeL_4(NO)]^+ + 2CNR \rightarrow [FeL_2(CNR)_2(NO)]^+ + 2L$$

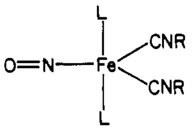
The reaction was also investigated by changing the molar ratio between the starting complexes and the isocyanide in the range 1–10, but in every case only formation of the bis(isocyanide) derivatives was observed.

The properties of these new complexes—all red-orange crystalline solids stable both in solid state and in solution—are given in Table I. The solids and solutions of these $\{Fe(NO)\}^8$ species are diamagnetic, and the conductivity values are typical of 1:1 electrolytes.[6]

The infrared spectra of the $[FeL_2(CNR)_2(NO)]^+$ derivatives show only one strong band at 1750–1767 cm^{-1} (CH_2Cl_2 solution) in the NO stretching frequencies, suggesting a linear MNO group for the complexes.[7] Furthermore, in the CN stretching region of the cations two strong bands at 2131–2141 and at 2080–2098 cm^{-1} (CH_2Cl_2 solution) appear, indicating a cis arrangement of the two isocyanide ligands.

In the temperature range +40 to −100 °C the $^{31}P\{^1H\}$ NMR spectra show only one singlet (Table I), revealing the existence of two magnetically equivalent phosphite ligands. Furthermore, the ^1H NMR spectrum of the $P(OMe)_3$ derivative shows a triplet at τ 6.08 in the phosphite methyl proton region, indicating that the two phosphite ligands are in the trans position.

The spectra of the $P(OEt)_3$ derivatives also agree with a trans arrangement. Therefore, on the basis of the reported data, a trigonal-bipyramidal geometry of the type II is proposed in solution for these complexes.



II

Table I shows that the ν(NO) frequencies of the isocyanide complexes are higher (15–33 cm^{-1}) than the corresponding frequencies of the $[FeL_4(NO)]^+$ derivatives, in agreement with a greater π-acceptor character of the isocyanides as compared to the phosphites. Furthermore, the ν(CN) frequencies in the $\{Fe[P(OEt)_3]_2(CNR)_2(NO)\}^+$ complexes depend on the nature of the substituent on the phenyl ring of the isocyanide ligand and change in the expected order. Surprisingly, the $2,6\text{-}(CH_3)_2C_6H_3NC$ derivative does not show a great difference in the ν(CN) as compared with the $4\text{-}CH_3C_6H_4NC$ derivative. In pentakis(isocyanide)iron(0) complexes[12] as well as in Co(I) isocyanide complexes,[13] the steric requirements of the 2,6-dimethyl isocyanide presumably explain the strong lowering in ν(CN) frequencies. In our case, the presence of the small NO group in the equatorial position (II) may explain the absence of the steric effect of the ortho-substituted isocyanide. Finally, methoxide ion is reported to attach $[Fe(PPh_3)_2(CO)_2(NO)]^+$ to a carbonyl carbon atom to give a methoxocarbonyl complex.[3a] In our case no reaction was observed by reacting the $[FeL_2(CNR)_2(NO)]^+$ (L = $P(OMe)_3$) complexes with either methoxide ion or amine, indicating that neither the CNR nor the NO ligands are susceptible to nucleophilic attack.

This behavior is perhaps not unexpected in view of the low ν(NO) and ν(CN) frequencies of these formal iron(0) complexes.

Experimental Section

Materials. Trimethyl and triethyl phosphite (Baker) were purified by distillation under nitrogen. Nitric oxide (Baker) was purified by passing it through a −80 °C trap. Substituted phenyl isocyanides were obtained by the phosgene method[14] of Ugi et al. All other organic reagents, solvents, and metal salts were reagent grade commercial materials. Organic solvents were purified by standard methods and distilled under a stream of nitrogen just prior to use.

Synthesis of the Complexes. All the preparative work was performed under an inert atmosphere by using standard Schlenk techniques. Once isolated, the complexes were shown to be stable in the air for 1–2 days.

$[FeL_4(NO)]BPh_4$ (L = $P(OMe)_3$, $P(OEt)_3$). To a solution of $FeBr_2$ (10 mmol, 2.17 g) in 80 mL of methanol or ethanol was added an excess of the appropriate phosphite (about 70 mmol), and the reaction mixture was stirred for 2 h. After filtration, nitric oxide was bubbled for 5 min through the solution, which was kept at room temperature under stirring for 30 min. The addition of $NaBPh_4$ (10 mmol, 3.15 g) and subsequent cooling at −30 °C induced the precipitation of red-brown product that was crystallized by methanol or ethanol; yield ≥40%.

Anal. Calcd for $\{Fe[P(OMe)_3]_4(NO)\}BPh_4$: C, 47.97; H, 6.26; N, 1.55. Found: C, 47.49; H, 6.08; N, 1.45. Mp: 151 °C. Λ_M: 58.0 $cm^2\ M^{-1}\ \Omega^{-1}$.

Calcd for $\{Fe[P(OEt)_3]_4(NO)\}BPh_4$: C, 53.89; H, 7.54; N, 1.31. Found: C, 53.43; H, 7.17; N, 1.31. Mp: 126 °C. Λ_M: 53.6 $cm^2\ M^{-1}\ \Omega^{-1}$.

$\{Fe[P(OEt)_3]_2(RNC)_2(NO)\}BPh_4$ (R = C_6H_5, $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$, $4\text{-}NO_2C_6H_4$, $2,6\text{-}(CH_3)_2C_6H_3$). A warm solution of $\{Fe[P(OEt)_3]_4(NO)\}BPh_4$ (1 mmol, 1.06 g) in ethanol containing 3 mmol of the appropriate isocyanide was refluxed under nitrogen for 3 h. After the warm solution had been filtered, the slow cooling to 4 °C caused the separation of red-orange crystals that were filtered, washed with ethanol, and dried under vacuum; yield ≥80%. The physical constants and the elemental analysis for the isocyanide complexes follow.

Anal. Calcd for R = C_6H_5: C, 63.64; H, 6.41; N, 4.45. Found: C, 63.00; H, 6.30; N, 4.13. Mp: 98 °C. Λ_M: 49.4 $cm^2\ M^{-1}\ \Omega^{-1}$.

Calcd for R = $4\text{-}CH_3C_6H_4$: C, 64.27; H, 6.64; N, 4.33. Found: C, 64.59; H, 6.51; N, 4.33. Mp: 57 °C. Λ_M: 52.2 $cm^2\ M^{-1}\ \Omega^{-1}$.

Calcd for R = $4\text{-}CH_3OC_6H_4$: C, 62.22; H, 6.43; N, 4.19. Found: C, 62.32; H, 6.26; N, 3.96. Mp: 59 °C. Λ_M: 52.3 $cm^2\ M^{-1}\ \Omega^{-1}$.

Calcd for R = $4\text{-}NO_2C_6H_4$: C, 58.10; H, 5.65; N, 6.78. Found: C 57.85; H, 5.30; N, 7.05. Mp: 115 °C. Λ_M: 50.2 $cm^2\ M^{-1}\ \Omega^{-1}$.

Calcd for R = $2,6\text{-}(CH_3)_2C_6H_3$: C, 64.87; H, 6.86; N, 4.20. Found: C, 64.96; H, 6.89; N, 4.12. Mp: 114 °C. Λ_M: 51.8 $cm^2\ M^{-1}\ \Omega^{-1}$.

$\{Fe[P(OMe)_3]_2(4\text{-}CH_3C_6H_4NC)_2(NO)\}BPh_4$. This complex was prepared following the method reported above using methanol as solvent and, to obtain crystals, by cooling the final solution to −30 °C; yield ≥70%.

Anal. Calcd: C, 62.25; H, 5.90; N, 4.74. Found: C, 61.91; H, 5.97; N, 4.46. Mp: 96 °C. Λ_M: 54.2 $cm^2\ M^{-1}\ \Omega^{-1}$.

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(11) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

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(13) Bordignon, E.; Croatto, U.; Mazzi, U.; Orio, A. *Inorg. Chem.* **1974**, *13*, 935.

(14) Ugi, I.; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offermann, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 472.

[$FeBrL_5$]BPh_4 (L = $P(OMe)_3$, $P(OEt)_3$).[15] The appropriate phosphite (60 mmol) was added to a solutoin of $FeBr_2$ (10 mmol, 2.17 g) in methanol or ethanol (80 mL). The reaction mixture was stirred for 2 h and added, after filtration, to a solution of $NaBPh_4$. After the solution was cooled to −30 °C, yellow crystals separated out in 1 day, which were filtered, washed with diethyl ether, and stored under vacuum at −20 °C; yield ≥60%.

Anal. Calcd for {$FeBr[P(OMe)_3]_5$}BPh_4: C, 43.56; H, 6.09. Found: C, 43.68; H, 6.23.

Calcd for {$FeBr[P(OEt)_3]_5$}BPh_4: C, 50.44; H, 7.45. Found: C, 50.12; H, 7.21.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 683 infrared spectrophotometer. Solid-state spectra were obtained from KBr pellets; solution spectra were obtained of potassium bromide cells. Proton magnetic resonance spectra were collected on a Varian EM 390 NMR spectrometer with tetramethylsilane as an internal standard. Fourier mode, proton noise decoupled phosphorus-31 NMR spectra were collected on a Varian FT 80A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Electron spectra were recorded on a Cary 219 spectrophotometer. Magnetic susceptibilities in solution were determined by the Evans method.[16] Conductivities of 10^{-3} M solution of complexes in nitromethane at 25 °C were measured with an "Halosis" bridge.

Acknowledgment. The financial support of the MPI and CNR, Rome, is gratefully acknowledged. We thank Daniela Baldan for her technical assistance.

Registry No. I·BPh_4 (L = $P(OEt)_3$), 91741-94-5; I·BPh_4 (L = $P(OMe)_3$), 91741-96-7; II·BPh_4 (L = $P(OEt)_3$, R = 4-$CH_3C_6H_4$), 91741-98-9; II·BPh_4 (L = $P(OEt)_3$, R = 4-$CH_3OC_6H_4$), 91742-00-6; II·BPh_4 (L = $P(OEt)_3$, R = 2,6-$(CH_3)_2C_6H_3$), 91742-02-8; II·BPh_4 (L = $P(OEt)_3$, R = 4-$NO_2C_6H_4$), 91742-04-0; II·BPh_4 (L = $P(OEt)_3$, R = C_6H_5), 91742-06-2; II·BPh_4 (L = $P(OMe)_3$, R = 4-$CH_3C_6H_4$), 91742-08-4; {$FeBr[P(OMe)_3]_5$}BPh_4, 70318-01-3; {$FeBr[P(OEt)_3]_5$}BPh_4, 70323-65-8.

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(15) These complexes have also been obtained by addition of phosphites to dihalobis(tetrahydrofuran)iron(II) complexes: Ittel, S. D.; English, A. D.; Tolman, C. A.; Jesson, J. P. *Inorg. Chim. Acta* **1979**, *33*, 101.

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Crystallographic Characterization of the Novel $(Ag_5Br_8)_n{}^{3n-}$ Polyanion

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In seeking to synthesize silver(I) analogues of the unusual 1:1 copper iodide:methyl isocyanide "displaced-stair polymer",[1] we have reacted silver(I) cyanide with excess alkyl halide/acetonitrile in sealed tubes at 100 °C for several days. One preparation involving *tert*-butyl bromide yielded a quantity of colorless highly crystalline (prismatic) material shown, by preliminary crystallographic examination, to have an unusually large unit cell. Subsequent structure determination, reported below, shows the presence of the novel $(Ag_5Br_8)_n{}^{3n-}$ polyanion.

Crystallography

Crystal Data: $C_{18}H_{42}Ag_5Br_8N_3O_3$, M_r = 1527, monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), a = 28.84 (1) Å, b = 6.350 (2) Å, c = 36.48 (1) Å, β = 108.25 (3)°, V = 6345 (3) Å^3. D_{calcd} (Z = 8) = 1.96 g cm^{-3}, $F(000)$ = 3620, monochromatic Mo Kα radiation, λ = 0.7106 6_9 Å, μ_{Mo} = 64 cm^{-1}. A^*_{min}, A^*_{max} = 1.46, 3.81. Specimen: 0.22 × 0.34 × 0.06 mm, T = 295 K.

Table I. Non-Hydrogen Atom Coordinates

atom	x	y	z
		Anion	
Ag(1)	0.4338 (1)	0.4499 (4)	0.65813 (8)
Ag(2)	0.4295 (1)	−0.0489 (4)	0.65337 (8)
Ag(3)	$^1/_2$	−0.0345 (7)	$^3/_4$
Br(1)	0.3520 (1)	0.6925 (6)	0.62731 (9)
Br(2)	0.4487 (1)	0.2038 (6)	0.60152 (9)
Br(3)	0.4191 (1)	0.1922 (6)	0.71254 (9)
Br(4)	0.5082 (1)	0.7153 (6)	0.69133 (9)
		Cation 1	
C(11)	0.6328 (9)	0.309 (6)	0.2602 (8)
C(12)	0.6726 (9)	0.447 (5)	0.2674 (8)
O(1)	0.6837 (6)	0.563 (3)	0.2421 (5)
N(1)	0.7020 (7)	0.471 (4)	0.3050 (6)
C(13)	0.7462 (9)	0.598 (5)	0.3218 (8)
C(14)	0.7819 (10)	0.564 (6)	0.2999 (9)
C(15)	0.7676 (11)	0.540 (7)	0.3624 (8)
C(16)	0.7324 (12)	0.838 (6)	0.3157 (11)
		Cation 2	
C(21)	0.0776 (10)	0.273 (5)	0.1853 (7)
C(22)	0.0941 (9)	0.112 (5)	0.1627 (8)
O(2)	0.1327 (6)	0.014 (3)	0.1764 (5)
N(2)	0.0669 (7)	0.086 (4)	0.1261 (5)
C(23)	0.0758 (11)	−0.061 (5)	0.0972 (7)
C(24)	0.0748 (13)	−0.282 (6)	0.1103 (8)
C(25)	0.0356 (13)	−0.005 (7)	0.0592 (9)
C(26)	0.1246 (11)	−0.023 (6)	0.0928 (9)
		Cation 3	
C(31)	0.8002 (11)	0.320 (5)	0.0707 (9)
C(32)	0.8085 (9)	0.415 (4)	0.0354 (7)
O(3)	0.7818 (7)	0.369 (4)	0.0014 (5)
N(3)	0.8414 (8)	0.561 (4)	0.0382 (7)
C(33)	0.8559 (12)	0.669 (5)	0.0079 (9)
C(34)	0.8975 (15)	0.817 (7)	0.0293 (10)
C(35)	0.8154 (12)	0.799 (6)	−0.0156 (11)
C(36)	0.8765 (15)	0.515 (6)	−0.0127 (11)

Structure Determination. A unique data set, measured to $2\theta_{max}$ = 50° on a Syntex P$\bar{1}$ four-circle diffractometer in conventional 2θ–θ scan mode, yielded 5371 independent reflections. Of these, 1706 with $I > 3\sigma(I)$ were considered observed and used in the full-matrix least-squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U)_H$ were included constrained at idealized values. Residuals at convergence (R, R') on $|F|$ were 0.053 and 0.062, reflection weights being $(\sigma^2(F_o) + 0.0005(F_o{}^2))^{-1}$. Neutral complex scattering factors[2] were employed; computation used the X-RAY 76 program system[3] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. No extinction correction was considered necessary.

Abnormal Features. Following the successful refinement of the heavy-atom component of the structure in terms of the $(Ag_5Br_8)_n{}^{3n-}$ species, residual difference map densities were modeled in terms of three *N*-*tert*-butylacetamide groups, necessarily protonated on stoichiometric grounds, presumably on the oxygen. The final refinement included all hydrogen atoms, except one of the oxygen that was regarded as ambiguous. Anisotropic refinement of the non-hydrogen atoms yielded a nonpositive definite thermal tensor (C(24)), probably a result of high cation thermal motion and limited data, rather than a deficient cation model; it should be noted, however, that cation

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(1) Fisher, P. J.; Taylor, N. E.; Harding, M. M. *J. Chem. Soc.* **1960**, 2303.

(2) Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham England, 1974; Vol. IV.

(3) Stewart, J. M., Ed. "X-RAY System", Technical Report TR-446; Computer Science Center: University of Maryland, College Park, MD, March 1976.

(4) The original structure determination of the $(Ag_2I_3)_n{}^{3n-}$ polyanion as the $[Me_4N]^+$ salt is reported in: Meyer, V. *Acta Crystallogr.* **1963**, *16*, 788. Data recorded in the present report is from: Kildea, J. D.; White, A. H., unpublished redetermination, 1983.

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