Figure 3. Spectral changes with time for CO binding to FeN$_4$A(CN)$^-$ in CO-saturated CH$_3$CN at 25 °C. Spectra 1–7 were recorded at times 0, 5, 10, 15, 25, 36, and 80 min.

from the analysis are also given in Table I. In the case of Br$^-$ no curvature in the plot is observed since K_{Br} is small; however, estimates of k_2 and K_{Br} can be made on the basis of data given below. For CN$^-$, eq 1 lies all the way to the right and only reaction 4 is observable (Figure 3).

It is important to note in the reaction at low [Cl$^-$] according to eq 3 that Cl$^-$ binding clearly precedes CO binding since Fe-N$_4$ACO does not react with Cl$^-$ on this time scale. The accelerated rate of CO binding in the presence of Cl$^-$ may be described as kinetic synergism. Thermodynamic synergism occurs with respect to the Cl$^-$ ligation since the extent of Cl$^-$ binding is much greater in the presence of CO (eq 3) than in its absence (eq 2).

The origin of this kinetic synergism is easily understood in terms of the well-established dissociative mechanism for ligand substitution in these complexes. Taking the most dramatic example of Cl$^-$, the pentacoordinate intermediate FeN$_4$A is more efficiently trapped by Cl$^-$ than by CO. Because Cl$^-$ is strongly trans labilizing for subsequent dissociation of A ($k_{-A}{}^{Cl} \gg k_{-A}{}^{A}$) the minor component, FeN$_4$ACl$^-$, reacts with CO much faster than the major component, FeN$_4$A$_2$, resulting in the reaction proceeding almost entirely[6] via the Cl$^-$-trapped intermediate.

The ratios of k_2 in Table I afford reasonable estimates of the relative trans effects on A lability. Relative to the previous estimate[3] of 1000 s^{-1} for $k_{-A}{}^{A}$, k_{-A} is approximately 10^7 s^{-1}, 3 × 10^5 s^{-1}, 8 × 10^3 s^{-1}, and 44 s^{-1} trans to Br$^-$, Cl$^-$, NCS$^-$, and CN$^-$, respectively.[7] The trans-effect order on CH$_3$CN lability correlates with the π-bonding properties of X$^-$ (π-donors labilizing and π-acceptors delabilizing).

The flash photolysis studies of FeN$_4$X(CO)$^-$ also provide data concerning the kinetics of eq 1. At low [X$^-$] the initial photoproduct, FeN$_4$AX$^-$, undergoes rapid dissociation of X$^-$ (reverse of eq 1) producing an equilibrium mixture of FeN$_4$A$_2$ and FeN$_4$AX$^-$. These reactions are much faster than those associated with CO ligation described above. For X = Cl$^-$, an increase in absorbance at 444 nm is observed after the flash independent of [CO] and with a dependence on [Cl$^-$] expected for the approach to equilibrium (eq 1) from the right. These data are collected in Table I. The rate constant for anion binding calculated from $k_f = K_X k_{-X}$ gives values of 1850 M^{-1} s^{-1} (Cl$^-$) and 1000 M^{-1} s^{-1} (NCS$^-$) in the range of rate constants found previously for the binding of neutral ligands.[3] Since the forward rates vary only

slightly with the nature of X$^-$, an estimate K_{Br} of ~0.1 M^{-1} may be made based on the value of k_{-Br} obtained in the flash experiments. The anionic complexes described here differ from Fe-(salen)[8] and heme[9] systems, which do not bind CH$_3$CN or CO and give pentacoordinate high-spin anionic complexes. In contrast, the low-spin FeN$_4$A$_2$ complex actually has a lower affinity for anions because a CH$_3$CN ligand must be displaced in eq 1.

The dramatic effects of anions reported here are relevant to reported CO ligation characteristics of lacunar systems described by Busch[10,11] and provide a simple model for synergistic (or cooperative) effects of ligation in biological systems.

Registry No. FeN$_4$A$_2$, 129194-53-2; [Et$_4$N][FeN$_4$(CN)(CO)], 137059-05-3; FeN$_4$ABr$^-$, 137059-06-4; FeN$_4$ACl$^-$, 137059-07-5; FeN$_4$A(NCS)$^-$, 137059-08-6; FeN$_4$A(CN)$^-$, 137059-09-7; FeN$_4$Br(CO)$^-$, 137059-10-0; FeN$_4$Cl(CO)$^-$, 137059-11-1; FeN$_4$(NCS)CO$^-$, 137059-12-2; FeN$_4$(CN)CO$^-$, 137059-04-2.

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Synthesis, Crystal and Molecular Structure, and Magnetic Properties of Bis[(μ-3,5-diamino-1,2,4-triazole-N^1,N^2)bis(μ-3,5-diamino-1,2,4-triazolato-N^1,N^2)triaquacobalt(II)]cobalt(III) Trichloride Nonahydrate

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1,2,4-Triazoles, Rtr, have been actively investigated as ligands capable of giving polymeric compounds with transition-metal ions and of effectively transmitting magnetic interactions between them.[2-9] In particular Reedijk et al. prepared series of trinuclear compounds of general formula [M$_3$(Rtr)$_6$(H$_2$O)$_6$]$^{6+}$, M = Mn, Fe, Co, Ni, and Zn, where Rtr is a substituted triazole. The exchange interaction has been found to be antiferromagnetic between the nearest-neighbor magnetic ions.[6-8] In these complexes the external ions are different from the internal one, and this allowed Reedijk et al. to observe a high-spin–low-spin transition of the central ion in a linear trinuclear iron(II) triazole compound.[6]

Despite the relatively large number of compounds containing triazoles so far isolated we are not aware of any trinuclear system with mixed-valence characteristics, although this possibility might

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(6) The carbonyl product is a kinetic (not thermodynamic) product under the conditions used. Product spectra are consistent with the amount of FeN$_4$A(CO) and FeN$_4$Cl(CO)$^-$ expected based on the relative rates of the k_1 and k_2 paths.
(7) These estimates consider the ratio k_1/k_2 (eqs 6 and 7) and assume k_{+A}/k_{+CO} is independent of the trans ligand.

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Table I. Crystallographic Data for [Co$_3$(dat)$_2$(datH)$_4$(H$_2$O)$_6$]Cl$_3$·9H$_2$O[a]

C$_{12}$H$_{56}$Co$_3$N$_{30}$O$_{15}$Cl$_3$	T = 25 °C
a = 10.333 (2) Å	λ = 0.71069 Å
α = 98.33 (1)°	ρ_{obsd} = 1.78 g/cm^3; ρ_{calcd} = 1.79 g/cm^3
V = 1064.65 Å^3	μ = 13.6 cm^{-1}
Z = 1	transm coeff = 1.00–0.94
mol wt 1144.94	$R(F_o)$ = 0.027
space group $R\bar{3}$ (C^2_{3i}, No. 148)	$R_w(F_o)^2$ = 0.029

[a] The unweighted and weighted residuals are defined as the following: R = $(\sum|F_o| - |F_c|)/\sum|F_o|$; R_w = $[\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$.

achieved by taking advantage of the difference between the central and external sites.

We have now synthesized bis[(μ-3,5-diamino-1,2,4-triazole-N^1,N^2)bis(μ-3,5-diamino-1,2,4-triazolato-N^1,N^2)triaquacobalt-(II)]cobalt(III) trichloride nonahydrate, [Co$_3$(dat)$_4$(datH)$_2$-(H$_2$O)$_6$]Cl$_3$·9H$_2$O, where datH = 3,5-diamino-1,2,4-triazole, which turned out to be a mixed-valence compound containing two cobalt(II) ions and one cobalt(III) ion, and we wish to report its structure and spectral and magnetic properties.

Experimental Section

Materials. Cobalt(II) chloride and 3,5-diamino-1,2,4-triazole (guanazole) were used as the commercially available compounds.

Synthesis. A water solution of datH and cobalt(II) chloride in 3:1 ratio which was left in the air for a few hours turned from yellow to brown. With very slow evaporation, crystals were obtained, which analytically were found to contain cobalt, ligand, and chlorine in 1:2:1 ratio. However at this stage it was not possible to be too much committed to the presence of deprotonated ligands. Therefore, we decided to undertake a complete X-ray single-crystal analysis in order to obtain a clear insight into the molecular structure.

Anal. Calcd for C$_{12}$H$_{56}$Co$_3$N$_{30}$O$_{15}$Cl$_3$: C, 12.60; H, 4.93; N, 36.73; Cl, 9.30. Found: C, 12.65; H, 4.98; N, 36.85; Cl, 9.65. Carbon, hydrogen, and nitrogen were determined with a Carlo Erba 1106 elemental analyzer, while chlorine was determined by the gravimetric method.

Spectral Measurements. The electronic spectrum of the solid compound was recorded as a mull transmission spectrum with a Cary 2300 Varian spectrophotometer. EPR spectra were recorded on a Varian E spectrometer on polycrystalline sample with diphenylpicrylhydrazyl (dpph, g = 2.0036) as the calibrating field marker.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measred in the range 4.2–300 K with a fully automatized AZTECDSM5 susceptometer equipped with an Oxford Instruments CF 1200S continuous-flow cryostat and a Bruker BE15 electromagnet, operating at ca. 1.2 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.

X-ray Structure Determination. The intensity data were collected at room temperature on a CAD 4 Enraf-Nonius automatic diffractometer. The crystals were shaped as irregular prisms. Details on crystal data, intensity collection, and structure refinement are reported in Table I. All data were corrected for Lorenz and polarization effects, and an empirical absorption correction, based on the ψ scan, was applied.[10]

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations, with $\sum_w(|F_o - F_c|)^2$ being minimized.

The observed Fourier map based on the converged isotropically refined trial structure using SHELX76[12] revealed two peaks in the closest proximity, suggesting a positional disorder, which can be explained in terms of a statistical alternative occurrence of Cl$^-$ or H$_2$O at two neighboring sites separated by 0.623 (7) Å. Least-squares refinement of their occupancy factors, with the sum constrained to unity, led to 0.459 (9) for the chlorine ion and 0.541 (9) for the water molecule. This corresponds to a total charge of 2.75. It means that the 70.83% of the guanazole molecules are deprotonated. Non-hydrogen atoms were treated anisotropically, whereas the H atoms were treated as fixed contributors at positions located from difference Fourier maps, assuming an isotropic temperature factor 1 Å^2 greater than that of the attached nitrogen atoms.

This model converged to R = 0.027 and R_w = 0.028, with w = 1.5/[$\sigma^2(F)$ + 0.0002F_o^2]. The residual electron density in the final difference

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Table II. Final Positional Parameters for [Co$_3$(dat)$_4$(datH)$_2$(H$_2$O)$_6$]Cl$_3$·9H$_2$O

atom	x/a	y/b	z/c
Co(1)	0.0	0.0	0.0
Co(2)	0.24223 (4)	0.24223 (4)	0.24223 (4)
C(1)	-0.1220 (3)	0.0046 (3)	0.2457 (3)
C(2)	0.0152 (3)	0.1438 (3)	0.3904 (3)
N(1)	-0.0244 (2)	0.0482 (2)	0.1849 (2)
N(2)	0.0668 (2)	0.1407 (2)	0.2807 (2)
N(3)	-0.1016 (2)	0.0617 (2)	0.3742 (2)
N(4)	-0.2370 (2)	-0.0831 (2)	0.1908 (2)
N(5)	0.0705 (3)	0.2223 (3)	0.5095 (2)
O(1)	0.2119 (2)	0.4188 (2)	0.3546 (2)
O(2)[a]	-0.637 (1)	-0.6603 (8)	-0.2686 (8)
O(3)	-0.3177 (3)	0.0218 (3)	0.5055 (4)
Cl(1)[a]	-0.6086 (4)	-0.6265 (3)	-0.3055 (3)

[a] O(2) and Cl(1) atoms have alternative occupancy factors of 0.5415 and 0.4585, respectively.
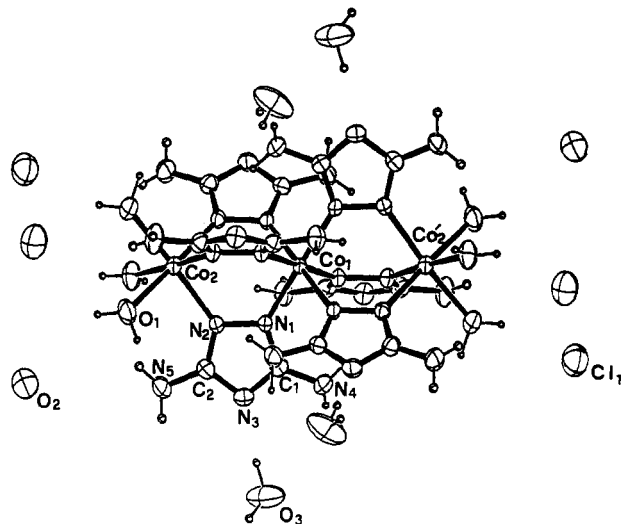

Figure 1. ORTEP view of the bis[(μ-3,5-diamino-1,2,4-triazole-N^1,N^2)-bis(μ-3,5-diamino-1,2,4-triazolato-N^1,N^2)triaquacobalt(II)]cobalt(III) trichloride nonahydrate complex, showing the atom numbering and thermal motion ellipsoids (50%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius. Two water molecules are omitted for clarity.

Fourier map was ±0.28 e Å^{-3}. Complex neutral-atom scattering factors[11] were employed throughout; major calculations were carried out on a Vax 6210 computer, using the SHELX76[12] program package and the ORTEP[13] plotting program.

Final fractional coordinates for non-hydrogen atoms are given in Table II.

Results and Discussion

The crystals are trigonal, and the structure consists of trimeric units with one cobalt in a $\bar{3}$ site symmetry and the other two in a 3 site symmetry. The trimer comprises six guanazole moieties and six water molecules.

The chlorine atoms randomly occupy six general positions in the cell, and so do three water molecules. Six other water molecules are clearly hydrogen bonded to the guanazole moieties.

In the trimeric cation the three cobalt ions are bridged by six guanazole moieties (Figure 1), as previously observed in trinuclear metal derivatives of 1,2,4 triazoles.[9] Each guanazole bridges two different cobalt ions with its 1,2-nitrogen atoms.

The central cobalt atom is bonded to six nitrogen atoms, with a very short distance of 1.965 (2) Å. The terminal cobalt ions on the other hand are bonded to three nitrogens, Co–N = 2.080 (2) Å, and to three water molecules, Co–O = 2.106 (2) Å. The latter distances compare well with those previously reported for cobalt(II) ions, while the former are much too short and suggest

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a cobalt(III) ion.[14] In fact the difference in the Co–N distances of the central and external metal ions, 0.115 Å, corresponds well to the difference in octahedral covalent radii of cobalt(II) and cobalt(III).[15]

We formulate the cation therefore as $[Co_3(dat)_4(datH)_2-(H_2O)_6]^{3+}$ and postulate that four guanazoles are deprotonated to guanazolate. This result is in line with the observed distance between nitrogen and terminal cobalt ion, which is slightly shorter than that observed in cobalt–triazole complexes.[16] A further confirmation comes from the electronic spectra, which show the $^4T_{1g} \rightarrow {}^4T_{2g}$ transition of octahedral cobalt(II) at 10 000 cm^{-1}. In analogous cobalt(II) complexes with protonated triazoles the corresponding band is observed[17] at 8500 cm^{-1} ca. The spectra show also a shoulder at ca. 17 000 cm^{-1} and a maximum at 21 000 cm^{-1}. The latter may be due to the $^4F \rightarrow {}^4P$ transitions of cobalt(II) and to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions of cobalt(III).

The distortion from ideal octahedral geometry of the coordination polyhedra solely involved the bond angles, whose deviations from ideal values are the same around the terminal and the central metal atoms (maximum of 4.1°).

The cobalt atoms are displaced from the mean planes through the triazole rings by 0.014 and 0.006 Å.

The Co(III)–Co(II) distance within the trimeric molecule is 3.653 (3) Å, lower than the 3.7121 (16)[18] and 3.828 (9)[16] Å found in the case of Co(II)–Co(II). The triazole rings are found to be planar within experimental error. Bond distances and angles of the ring compare well with those found by other authors.[6,8] The dihedral angles between the ring planes are 60.0°.

Intermolecular hydrogen-bond contacts, on which the crystal packing mainly depends, occur among the water molecules, the NH_2 and NH groups of the 2,5-diamino-triazole molecules, and the chloride ions. The results of the refinement of the disordered chlorides and water molecules appear to indicate that ca. 46% of chlorine and ca. 54% of water oxygen is present in the compound. This means that, with chlorine ions present (as in **1**), the water

1   **2**
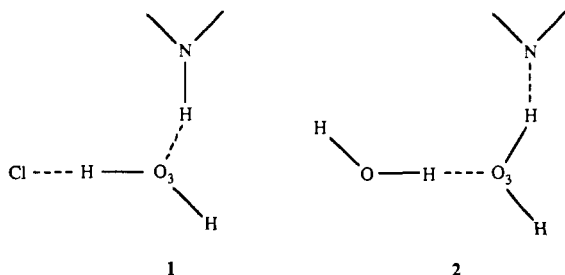
molecule O(3) is oriented such that one proton hydrogen bonds to the Cl$^-$ ion, while the protonated ligand hydrogen bonds to O(3). In contrast, when a water molecule O(2) replaces the Cl$^-$ ion, the O(3) water molecule reorients so that hydrogen bonding depicted in **2** occurs; e.g., the O(2) water molecule hydrogen bonds to O(3), while the O(3) water molecule now hydrogen bonds to the deprotonated N atom on the ligand.

Magnetic Properties. The magnetic properties of $[Co_3-(dat)_4(datH)_2(H_2O)_6]Cl_3\cdot9H_2O$ agree with the formulation $Co^{II}_2Co^{III}$. In fact the room-temperature effective magnetic moment, $\mu_B = 7.15$, agrees well with the presence of two uncoupled high-spin octahedral cobalt(II) ions each with $\mu_{eff} = 5.1$ μ_B, while it would be too small for three cobalt(II) ions, each with $\mu_{eff} = 5.1$ μ_B. In fact the range of μ_{eff} values for octahedral cobalt(II) ions is 4.8–5.4 μ_B. Further the temperature independence of χT down to ca. 100 K rules out any possibility of relevant antifer-

romagnetic interaction which might in principle reduce the room-temperature effective magnetic moment. The observed decrease of χT at lower temperature can be attributed to the thermal depopulation of the excited Kramers's doublets originated by spin–orbit and low-symmetry splitting of $^4T_{1g}$ of the two cobalt(II) ions. Below 20 K μ_{eff} stabilizes to 5 μ_B, which agrees with two uncoupled effective $S = {}^1/_2$ spins with $g = 4.1$.

The polycrystalline powder EPR spectra recorded at 4.2 K are axial, with $g_\parallel = 8.8$ and $g_\perp = 1.5$. These values compare well with those observed in octahedral high-spin cobalt(II)[19] and show that the two ions are substantially uncoupled. Further, the fact that only one set of signals is observed rules out the presence of a third cobalt(II) ion.

Conclusion. In conclusion, $[Co_3(dat)_4(datH)_2(H_2O)_6]Cl_3\cdot9H_2O$ is the first example of mixed-valence trinuclear cobalt derivative with 1,2,4-triazoles. All the evidence is that the valences are effectively trapped. The analysis of the magnetic data provided evidence that the coupling between the external cobalt(II) ions is indeed very weak, thus solving a long debated problem[20] in the analysis of the magnetic properties of trinuclear cobalt(II) complexes.

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Contribution from the Institute of Organo-Element Compounds, USSR Academy of Sciences, Moscow, USSR, and Department of Chemistry, Moscow State University, Moscow, USSR

Reactions of Aryl(B-carboranyl)iodonium Cations with the Fluoride Anion. Synthesis of Icosahedral o-Carboran-9-yl, m-Carboran-9-yl, and p-Carboran-2-yl Fluorides

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Introduction

Hundreds of different icosahedral *closo*-carborane(12) derivatives containing boron–element bonds (element = halogen, nitrogen, carbon, oxygen, sulfur, main-group and transition metals, etc.) have been synthesized over the last 25–30 years.[1] Direct electrophilic chlorination, bromination, and iodination is known to be an effective and convenient method for the preparation of boron halogenated *o*-, *m*-, and *p*-carboranes.[2] Similarly, selective

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