ing one-third of the cobalt (either in interstitial sites or nitrogen holes) has a calculated magnetic moment of 4.90 BM. This is close to the value calculated for the high-spin cobalt in the unisomerized material, as it should be. Accordingly, we write

$$\mathrm{Co^{2+}(NC)_6Cr^{III}} \xrightarrow{\Delta,\ \mathrm{O_2}} \mathrm{Cr^{3+}(NC)_6Co^{III}}$$

for the over-all reaction.

In previous work on the site-interchange reactions of $\mathrm{Fe[Cr(CN)_6]_2}$,[9] it was found that the reaction proceeded in a stepwise fashion, and it may be inferred that the isomerization mechanism involves a movement of metal ions between carbon-coordinated, interstitial, and nitrogen-coordinated sites. In the present study no evidence for intermediates was found. This leaves open the question of the mechanism; however, one simple explanation of the present results is that this reaction occurs by an end-for-end flip of the C≡N groups.

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The Environment of Interstitial Ions in a Prussian Blue Analog, $\mathrm{Co_3[Co(CN)_6]_2}$

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Magnetic data indicate that interstitial $\mathrm{Co^{2+}}$ is present as a high-spin octahedral complex in the pink solid $\mathrm{Co_3[Co(CN)_6]_2 \cdot}$ $x\mathrm{H_2O}$. Visible and infrared spectra of this pink hydrate, along with changes in these spectra and of magnetic moments upon dehydration, indicate the octahedral interstitial complex is $\mathrm{Co(H_2O)_6^{2+}}$. Previous pressure–composition studies on similar Prussian blue analogs are discussed. Contrary to an earlier interpretation, a smooth decrease in pressure with decreasing water content does not imply the absence of discrete species such as $\mathrm{M(H_2O)_6^{2+}}$. Since $\mathrm{NH_3}$ should form a stronger complex than water and adsorb less readily, a study was carried out on the system $\mathrm{NH_3}$–$\mathrm{Co_3[Co(CN)_6]_2}$. The absorption isotherms demonstrate the existence of $\mathrm{Co_3[Co(CN)_6]_2 \cdot 6NH_3}$, for which stoichiometry and infrared data indicate the presence of $\mathrm{Co(NH_3)_6^{2+}}$ interstitial complexes.

Introduction

In Prussian blue and its numerous analogs, nitrogen-coordinated and carbon-coordinated metal ions occur in a 1:1 ratio. X-Ray powder diffraction and, to some extent, spectroscopic data show that the nitrogen- and carbon-coordinated metals are in regular octahedral environments.[3-10]

A third type of metal ion (which we call interstitial) is generally present to maintain electroneutrality of the Prussian blue analog. For example, the compound $\mathrm{Co_3[Co(CN)_6]_2}$ contains two nitrogen-coordinated, two carbon-coordinated, and one interstitial cobalt atoms. By contrast to the N- and C-coordinated metal ions, the first coordination sphere for interstitial ions is quite uncertain.

From the X-ray powder diffraction studies of Weiser, Milligan, and Bates[5] and of subsequent workers, it appears that the interstitial ions are distributed in a random fashion over the eight sites of $\bar{4}3m$ (T_d) symmetry in the unit cell (space group Fm3m). This site is illustrated in Figure 1 where it may be seen that there are no groups within bonding distance of the interstitial metal ion. The shortest distance is *ca.* 3.5 Å from the ion to one edge of the octant, that is, to the axis of the C≡N group. Individual C and N atoms are even further removed. Actually, this energetically unfavorable situation may not exist because water which is generally present in these compounds conceivably may be coordinated to the metal ions. Indeed, coordination by water was proposed in a number of early reports.[3,11] However, somewhat more recent studies of the partial pressure of water *vs.* composition were interpreted in terms of adsorption with no specific chemical interaction.[12]

The present detailed investigation of $\mathrm{Co_3[Co(CN)_6]_2}$ was designed to clarify the nature of the interstitial species in a typical Prussian blue analog. This par-

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[3] J. F. Keggin and F. P. Miles, *Nature*, **137**, 577 (1936).

[4] For a summary of Prussian blue analogs see D. F. Shriver, *Struct. Bonding* (Berlin), **1**, 32 (1967).

[5] H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, **46**, 99 (1942).

[6] M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

[7] P. S. Bratterman, *J. Chem. Soc. A*, 1471 (1966).

[8] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **4**, 725 (1965).

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[10] E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 277 (1963).

[11] A. K. van Bever, *Rec. Trav. Chim.*, **57**, 1259 (1938).

[12] H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, **45**, 401 (1941); see also K. Maer, Jr., M. L. Beasley, R. L. Collins, and W. O. Milligan, *J. Am. Chem. Soc.*, **90**, 3201 (1968).

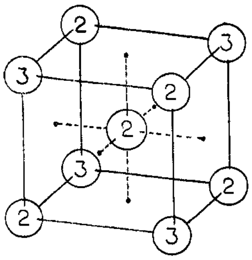

Figure 1.—Interstitial site in $Co_3[Co(CN)_6]_2$: (3) Co(III); (2) Co(II); CN groups lie along the solid lines with the carbon ends toward Co(III). The central Co(II) atom is in an interstitial position of $\bar{4}3m$ symmetry.

ticular compound was chosen for study because it was found to undergo a fully reversible pink to blue transformation upon dehydration,[13] which logically may be attributed to changes in the degree of aquation of interstitial cobalt(II).

Experimental Section

$Co_3[Co(CN)_6]_2$ was prepared by the slow addition of an aqueous solution of $K_3Co(CN)_6$ to an excess of $CoSO_4$ solution. The product was collected by centrifugation and washed with absolute alcohol. This wash produces a blue solid which becomes pink after long exposure to atmospheric moisture. (Earlier preparations by S. A. Shriver, performed without the alcohol wash, were pink when wet and blue when dry.[13b]) Cobalt was determined by igniting the sample and weighing the residue as Co_3O_4. The purity of this oxide was established by a thiocyanate colorimetric analysis.[14] Nitrogen was determined by Miss Hilda Beck, using an F & M carbon, hydrogen, and nitrogen analyzer, Model 185, which yields unusually accurate nitrogen analyses with cyanide compounds. Average values for several determinations on the pink hydrate which had been equilibrated with atmospheric moisture are: N, 18.75%; Co, 32.98%. The resulting nitrogen to cobalt ratio is 2.40, exactly the value expected for the hydrate of $Co_3[Co(CN)_6]_2$.

Standard chemical high-vacuum practice was employed in the determination of the NH_3–$Co_3[Co(CN)_6]_2$ pressure–composition isotherms.[15] The ammonia was Matheson anhydrous grade which was fractionated through a −78° trap prior to use; vapor pressure at −45.21°, 408 mm; lit.[15] value, 408 mm.

Display infrared spectra were recorded for Nujol mulls between KBr plates using a Beckman IR-10. These were prepared for Figure 2 by direct tracing with slight smoothing at order breaks and filter changes. Precise values for band positions were determined on Beckman IR-9 and IR-11 instruments. Visible spectra were determined on a Cary 14 for Nujol mulls sandwiched between fused-quartz plates. Mulls of $Co_3[Co(CN)_6]_2 \cdot 6NH_3$ and dehydrated blue $Co_3[Co(CN)_6]_2$ were prepared in a nitrogen-flushed glove bag. The dehydrated blue compound was generated by subjecting the pink hydrate to high vacuum at 90° for 14 hr.

Magnetic susceptibilities were determined on a Faraday balance which is described elsewhere.[16] Three separate determinations were performed on both the pink and the blue forms. These were found by first measuring the pink compound and then heating the sample to 110° in a dry helium stream until constant weight was achieved, which was taken as an indication of complete conversion to the blue form. In each run, measurements were made at 8–13 temperatures from −149 to +27° for the pink form and −42 to +114° for the blue. X-Ray powder photogaphs were obtained with a 57.3-mm Debye–Scherrer camera using vanadium-filtered Cr Kα radiation, λ 2.2909 Å. Films were processed quickly to minimize film shrinkage and no shrinkage correction was applied.

Results and Discussion

Magnetic and Visible Spectral Data for $Co_3[Co(CN)_6]_2 \cdot xH_2O$.—As mentioned in the previous two sections, $Co_3[Co(CN)_6]_2 \cdot xH_2O$ undergoes a reversible color change from pink to blue upon dehydration. This change occurs without any change in the basic framework, since both forms are face-centered cubic and have unit cell parameters which are identical within experimental error (pink, 10.17 Å; blue, 10.16 Å). Similarly the infrared spectrum in the C≡N stretch region is only slightly changed by dehydration (pink: 2177 s, 2139 w cm^{-1}; blue: 2183 s cm^{-1}). Since dehydration does not affect the framework of this compound, it is logical to associate the color change with interstitial ions.

Visible spectra reveal a broad maximum at *ca.* 470 mμ (*ca.* 21,000 cm^{-1}) for the pink compound and a sharper, more intense absorption at *ca.* 585 mμ (*ca.* 17,000 cm^{-1}) for the blue material. The band in the pink material is reasonably assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition of octahedrally coordinated Co^{2+} which is found near 20,000 cm^{-1} in $Co(H_2O)_6^{2+}$.[17] Since nitrogen-coordinated Co^{2+} is present in twofold excess over the interstitial species, this spectrum may be interpreted in terms of a composite of absorptions due to $Co^{2+}(NC)_6$ and $Co(H_2O)_6^{2+}$. It is known that the nitrogen end of cyanide is slightly higher on the spectrochemical series than water,[8] so the observed position is in harmony with this interpretation.

More conclusive evidence for an octahedrally coordinated interstitial Co^{2+} is obtainable from magnetic data. The average susceptibility for the pink material (in cgs units) is $\chi_g(\text{pink}) = 10.61 \times 10^{-3}/(T + 16)$. Based on the formulation $Co_3[Co(CN)_6]_2$, two-fifths of the cobalt is present as Co(III) in carbon holes and consequently is diamagnetic. By using the analytical data and treating the remaining three-fifths of the cobalt (*i.e.*, Co^{2+}) as magnetically equivalent, one calculates a moment of 4.95 BM for the Co^{2+} at 300°K. This result is in excellent agreement with our expectation for the presence of $Co(H_2O)_6^{2+}$ in addition to $Co^{2+}(NC)_6$, since octahedral Co^{2+} is generally found in the range 4.9–5.0 BM.[18]

It is tempting to attribute the pink to blue transformation to a change from $Co(H_2O)_6^{2+}$ interstitial ions to a tetrahedral Co^{2+} interstitial species. (It should be noted that the band observed at 17,000 cm^{-1} in the blue material is sufficiently broad and intense to obscure absorptions which are expected for octahedral Co^{2+} in nitrogen holes.) The position, shape, and apparent intensity of the absorption maximum for the blue material are in qualitative agreement with the

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[13] (a) D. B. Brown and D. F. Shriver, *Inorg. Chem.*, **8**, 37 (1969); (b) S. A. Shriver, unpublished observations, Northwestern University, 1964.

[14] A. R. Olson, C. W. Koch, and G. C. Pimentel, "Introductory Quantitative Chemistry," W. H. Freeman and Co., San Francisco, Calif., 1956, pp 426–432.

[15] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., in press.

[16] D. B. Brown, D. F. Shriver, and L. H. Schwartz, *Inorg. Chem.*, **7**, 77 (1968). Gram susceptibilities are quoted on the basis of the initial weight of complex.

[17] O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

[18] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 185 (1964).

known intense absorption of tetrahedral Co^{2+}. For example, the intense $^4A_2 \rightarrow {}^4T_1(P)$ band of $CoCl_4^{2-}$ is found near 15,000 cm^{-1}.[19] However, the magnetic data and vibrational data (described later) leave the exact nature of this interstitial Co^{2+} uncertain.

Since the magnetic moment for tetrahedral Co^{2+} generally falls in the range 4.5–4.7 BM,[18,19] a decrease in susceptibility should accompany the pink to blue transformation. Qualitatively the expected decrease is observed, since $\chi_g(\text{blue}) = 9.26 \times 10^{-3}/(T + 9)$. However, the quantitative moment which may be derived for the interstitial cobalt is unusually low. This moment is found by assigning a magnetic moment to the nitrogen-coordinated cobalt which is identical with that determined for the pink form, and a value for the susceptibility of $Co^{2+}(NC)_6$ at 300° is calculated and subtracted from $\chi(\text{blue})$, while the usual diamagnetic susceptibility corrections are added. The resulting susceptibility yields a moment of 3.9 BM for the interstitial Co^{2+}, which is 0.6 BM below the expected value for a tetrahedral complex.

Absorption Isotherms.—Previous studies on the pressure–composition isotherms for several Prussian blue analogs have yielded smooth curves which were interpreted in terms of adsorption on surfaces and channels rather than definite chemical combination.[12] While $Co_3[Co(CN)_6]_2$ was not included among the compounds studied, a number of very similar compounds containing interstitial transition metals were investigated.

The apparent conflict between this interpretation and ours may be resolved by recalling that dehydration has little effect on the rigid metal cyanide framework and does not lead to the formation of a new phase with a concomitant reduction in the degrees of freedom available to the system. Similarly it is found that substitution of alkali metal ions for interstitial transition metal ions has little effect on the lattice parameter for a particular Prussian blue analog.[4,13a] Therefore, it is reasonable to view the solid as a solution of interstitial ions in a rigid metal–cyanide framework.[20] Even though this solid may contain discrete interstitial species such as $M(H_2O)_6^{2+}$, the entropy and free energy of desorption per mole of water will be a strong function of gross composition, quite unlike the situation where desorption leads to a new phase.

Some specific desorption steps which are likely for a solid of the type under consideration are dissociation of interstitial complexes

$$Co(H_2O)_6^{2+}(\text{interstitial}) = Co(H_2O)_5^{2+}(\text{interstitial}) + H_2O(g)$$
$$Co(H_2O)_5^{2+}(\text{interstitial}) = Co(H_2O)_4^{2+}(\text{interstitial}) + H_2O$$

and vaporization of adsorbed water

$$H_2O(\text{monolayer}) = H_2O(g)$$
$$H_2O(\text{bimolecular layer}) = H_2O(g)$$

If we employ the BET formalism, the pressure of water due to the ith adsorbed layer is[21]

$$P_i = A_i X_i e^{-\Delta H_i/RT} \qquad (1)$$

where A_i is a constant, X_i is the mole fraction of surface coverage in the ith layer, and ΔH_i is the heat of vaporization for 1 mol of water in the ith layer. Assuming ideal behavior for the nth hydrate, $M(H_2O)_n^{m+}$, an exactly analogous expression may be written

$$P_n = A_n X_n e^{-\Delta H_n/RT} \qquad (2)$$

where A_n is a constant, X_n is the mole fraction of interstitial cobalt present in the nth hydrate, and ΔH_n is the heat of reaction for

$$M(H_2O)_n^{m+}(\text{interstitial}) = M(H_2O)_{n-1}^{m+}(\text{interstitial}) + H_2O(g)$$

It is instructive to consider several limiting conditions. When the heat of formation of the monolayer is comparable to that of the last complex-forming step, $\Delta H_i \sim \Delta H_n$, a distinct inflection in the pressure curve will not appear at the composition $Co_3[Co(CN)_6]_2 \cdot 6H_2O$. This type of smooth isotherm has been classified as type III for adsorption phenomena.[22] When $\Delta H_i < \Delta H_n$, complex formation is favored over adsorption and a break may be evident in the adsorption isotherm (type IV isotherm).[22]

A reasonable lower limit to the heat of vaporization of water molecules from an interstitial complex is 10.9 kcal/mol of water which was determined for[23]

$$[Ni(H_2O)_6]SO_4(s) = Ni(H_2O)_4SO_4(s) + 2H_2O(g)$$

For a lower limit to the heat of desorption of a water monolayer on Prussian blue, we employ the heat of vaporization of water which is 10.5 kcal/mol at 25°. These numbers indicate but certainly do not prove that $\Delta H_i \sim \Delta H_n$. Thus, a featureless adsorption isotherm (type III) is reasonable for hydrates of the Prussian blue analogs, even though these hydrates may contain discrete aquo complexes of the interstitial ions.

$Co_3[Co(CN)_6]_2$–NH_3 System.—Studies on this system were prompted by our expectation that complex formation should predominate over adsorption (*i.e.*, $\Delta H_i < \Delta H_n$). As illustrated in Table I, a distinct break is observed in the ammonia pressure at the composition $Co_3[Co(CN)_6]_2 \cdot 6NH_3$, for data collected at 22.5 and 0°. This is exactly the composition expected for complete conversion of the interstitial cobalt(II) to $Co(NH_3)_6^{2+}$. In addition, the data just below the 1:6 ratio at 23° show that the vapor pressure of the interstitial complexes is a function of gross composition. This observation is in qualitative agreement with the expectation that the pressure increases with an increase in the mole fraction of each hydrated species, *i.e.*, eq 2.

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(19) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

(20) Additional support for this model is afforded by the X-ray data which indicate the interstitial ions are disordered (*e.g.*, ref 3–5).

(21) S. Brunauer, P. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

(22) S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *ibid.*, **62**, 1723 (1940).

(23) A. Solomon and N. Knauer, *Z. Anorg. Allgem. Chem.*, **242**, 375 (1939). This value is a lower limit because the formation of a new solid phase (the tetrahydrate) will involve a lattice energy contribution which does not have an exact analog in the Prussian blue system where a second solid phase is not formed.

TABLE I

PRESSURE–COMPOSITION DATA FOR THE SYSTEM NH_3–$Co_3[Co(CN)_6]_2$

22.5°		0°	
n/n_0[a]	P, mm	n/n_0[a]	P, mm
1.67	0.0		
3.81	0.0		
4.09	0.1		
4.94	0.5	5.36	0.0
5.30	1.3	5.58	0.3
6.00	3.2	6.08	0.7
6.34	15.4	6.42	4.9
6.85	41.2	6.99	21.9
6.89	55.3	7.32	32.4

[a] Moles of NH_3 in condensed phase divided by moles of anhydrous $Co_3[Co(CN)_6]_2$.

Upon absorption of ammonia, the blue dehydrated $Co_3[Co(CN)_6]_2$ is converted to a pink compound. The visible spectrum of $Co_3[Co(CN)_6]_2 \cdot 6NH_3$ contains a shoulder at *ca.* 455 mμ, which as expected represents a blue shift from the 470-mμ $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ absorption of the hydrate. The blue shift results from the position of NH_3 higher on the spectrochemical series than H_2O. Additional and much more conclusive evidence for an interstitial $Co(NH_3)_6^{2+}$ was obtained from medium- and far-infrared spectra.

Medium- and Far-Infrared Spectra.—Display spectra for blue dehydrated $Co_3[Co(CN)_6]_2$, the pink hydrate, and the hexaammine are presented in Figure 2. The blue material shows virtually no absorption in the 3500- and 1600-cm^{-1} regions, which are characteristic of water. We conclude that this material is nearly anhydrous and therefore an interstitial species such as $Co(H_2O)_4^{2+}$ is unlikely. The first coordination sphere of interstitial cobalt in the dehydrated material is not clear. It will be recalled that the magnetic moment is significantly lower than expected for a tetrahedral species. It is probable that the cobalt ion is in close proximity to the C≡N groups which serve as π-type ligands. In this fashion it would be possible to satisfy up to three coordination sites on the metal, as shown in Figure 3. While the interstitial ion no longer resides at the $\bar{4}3m$ sites, a random orientation of the ions in the various octants will probably have little influence on the structure factors. Therefore, the proposed structure appears to be compatible with the nearly identical powder patterns observed for the hydrous and dehydrated forms.

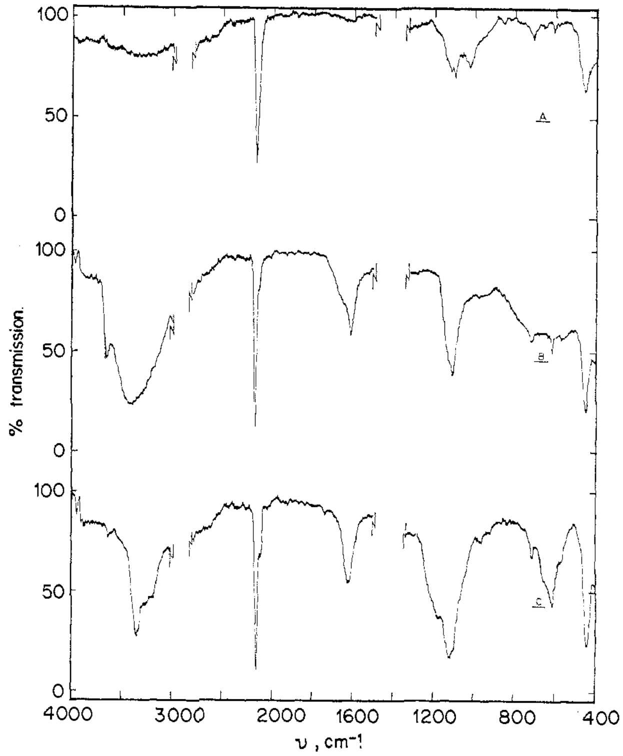

Figure 2.—Infrared spectra of: A, $Co_3[Co(CN)_6]_2$, blue dehydrated form; B, $Co_3[Co(CN)_6]_2 \cdot xH_2O$, pink hydrated form; C, $Co_3[Co(CN)_6]_2 \cdot 6NH_3$. Except for a weak band at *ca.* 720 cm^{-1} all Nujol bands have been deleted.

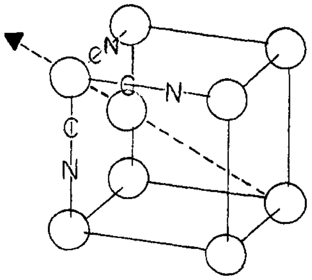

Figure 3.—Possible environment of Co^{2+} in dehydrated $Co_3[Co(CN)_6]_2$. The central Co^{2+} has been displaced along the threefold axis.

Several features in the infrared spectrum are consistent with a reduction in symmetry upon dehydration. It is clear from Figure 2 that the absorption around 1100 cm^{-1} in the pink hydrate and hexaammine is split into two groups of bands in the dehydrated material. While the exact assignment for this band system is in doubt, the frequency is indicative of C≡N motions, possibly a C≡N deformation which has been greatly increased in frequency over a similar vibration of terminal C≡N groups in simple hexacyanometalates. In any case, the splitting of this absorption upon dehydration indicates a lowering of symmetry, as expected for a π type of C≡N metal interaction. While the C≡N stretch frequency at 2177 cm^{-1} of the aquated compound is only slightly shifted to 2183 cm^{-1} upon dehydration, there is a significant increase in peak width at half-height from 35 to 50 cm^{-1} in the respective compounds. Again this may be attributed to a perturbation of C≡N motions by a π metal–cyanide interaction. However, Farona and Bremer observed a 185-cm^{-1} decrease in ν(CN) upon formation of a nitrile–manganese(I) π complex.[24] We conclude that even though the π-complex structure seems to be a plausible structure for the dehydrated material, the evidence is not conclusive.

The spectrum of the pink hexaammine is in good agreement with expectation for a $Co(NH_3)_6^{2+}$ species. The frequencies along with assignments are presented in Table II, and a display spectrum is given in Figure 2. From the comparison with literature data for a known

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(24) M. B. Farona and N. J. Bremer, *J. Am. Chem. Soc.*, **88**, 3735 (1966).

TABLE II

INFRARED SPECTRA[a]

$Co_3[Co(CN)_6]_2 \cdot 6NH_3$ pink ammoniate	$[Co(NH_3)_6]Cl_2$[b]	$Co_3[Co(CN)_6]_2$ blue dehydrate[d]	Assignment[c]	$Co_3[Co(CN)_6]_2 \cdot xH_2O$ pink hydrate[d]
3355 s	3330			3650 m
Ca. 3280 sh	3250		$\nu(NH_3)$	3400 s
Ca. 3187 sh				
2166 s		2183	$\nu(CN)$	2177 s
2125 sh				2139 w
1624 m	1605		$\delta(NH_3)$	1660 sh
				1610 mw
1187 m	1160		$\delta(NH_3)$	
		Ca. 1150 sh		
1129 m		1140 ms		1135 m
		1111 s		1105
		Ca. 1033 ms		
		873 mw		
Ca. 645 sh	634		$\rho(NH_3)$	615
609 ms				
		619 w		
Ca. 575 sh		517 sh		
444 s		492 sh	$\nu(MC)$	495 sh
		440 s		460 m
312 ms	318		$\nu(MN)$	
Ca. 287 sh				
242 s		230 mw		228 mw
202 s	192		$\delta(H_3NCoNH_3)$	

[a] All frequencies are in cm^{-1}: s, strong; m, medium; w, weak; sh, shoulder; ν, stretch; δ, deformation; ρ, rock. [b] From I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22,** 759 (1966). [c] Assignments for NH_3 frequencies apply to the first two columns. [d] Except for $\nu(CN)$ and bands below 500 cm^{-1}, these frequencies were determined with a Beckman IR-10 and are less accurate than other entries in the table, which for sharp bands are known to *ca.* ±1 cm^{-1} for 4000–400 cm^{-1} and *ca.* ±3 cm^{-1} for 400–100 cm^{-1}.

hexamminecobalt(II) complex it is clear that this species is present in $Co_3[Co(CN)_6]_2 \cdot 6NH_3$. The principal disparities occur in the NH_3 stretching and deformation regions which are known to be highly sensitive to environment.[25] However, comparison with the spectrum of dehydrated $Co_3[Co(CN)_6]_2$ leaves no doubt about the assignments. Of particular importance in establishing the presence of a coordinated NH_3 is the rocking frequency at *ca.* 645 cm^{-1}, which appears to underlie a weak, sharp unassigned peak at *ca.* 609 cm^{-1} (see Figure 2C). Of similar importance are bands at 312 and 202 cm^{-1} which are, respectively, assigned to Co–N stretch and N–Co–N deformation frequencies of $Co(NH_3)_6{}^{2+}$.

The spectrum of the pink aquated $Co_3[Co(CN)_6]_2 \cdot xH_2O$ contains bands which may be interpreted in terms of $Co(H_2O)_6{}^{2+}$. However, the vibrational spectra do not conclusively demonstrate the presence of the hexaaquo species. The H_2O stretch and deformation frequencies are evident around 3400 and 1610 cm^{-1} (Table II and Figure 2B). It is known that these particular frequencies are even more dependent upon environment than NH_3 stretches and deformations; however, the observed positions are in general agreement with other hexaaquo complexes of divalent metals. A broad absorption extending from *ca.* 720–580 cm^{-1} (see Figure 2B) encompasses the region of H_2O rock and wag vibrations.[26] Unfortunately, the asymmetric Co–O stretch was not located in the infrared spectrum. Presumably this is due to the known low intensity and breadth of this type of absorption[26] coupled with the presence of other bands in the vicinity of 400 cm^{-1}. Attempts to locate the totally symmetric Co–O stretch by means of laser Raman spectroscopy on a pressed disk were unsuccessful owing to local dehydration of the sample by the focused laser beam. This dehydration was evidenced by a transient blue spot in the pellet at the point the laser beam impinged on the sample.

In summary, a variety of physical data indicate that in the presence of water or ammonia ligands the interstitial Co^{2+} in $Co_3[Co(CN)_6]_2$ occurs as an octahedral complex.[27] It is probable that this is a general phenomenon for interstitial transition metal ions in all Prussian blue analogs.

Many previous observations on Prussian blue analogs are straightforwardly explained by the occurrence of interstitial $M(H_2O)_6{}^{n+}$ species. For example, Keggin and Miles noted that the presence of interstitial transition metal ions is associated with high water content.[3] Also, Mössbauer studies indicate that the recoil-free fraction is approximately equal for carbon-coordinated, nitrogen-coordinated, and interstitial iron ions.[9,10,12,16] This observation is in harmony with the binding of the interstitial iron ions by water. Finally, magnetic studies on a wide variety of Prussian blue analogs may be interpreted in terms of octahedrally coordinated interstitial ions.[13a]

Acknowledgment.—This work was supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern Materials Research Center. We thank Professor R. L. Burwell for informative discussions of adsorption phenomena.

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(25) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 143 ff.

(26) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 429 (1964).

(27) It appears that there is sufficient room for the hexaaquo or hexaammine complexes in interstitial sites. The required nonbonded distances may be estimated as follows. H_2O or NH_3 ligands are placed along the dotted lines in Figure 1 and allowed to approach the cobalt at the known Co—N distance [M. T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Commun.*, 307 (1966)] or estimated Co—O distance. Also, the lattice parameter for $Co_3[Co(CN)_6]_2$ is employed along with known $Co—C\equiv N$ distances. For the interstitial hexaammine these figures yield *ca.* 2.6 Å for N · · · N and C · · · N contacts between NH_3 and CN, while the shortest possible H · · · N distance between NH_3 and CN is calculated to be *ca.* 1.7 Å. Similar distances are estimated for the hexaaquo complex. For comparison, the sum of van der Waals radii varies from 2.4 to 3.0 Å for N · · · N and from 2.7 to 3.1 Å for N · · · C, depending on the source of the radii, while the O · · · N and O · · · C distances are about 0.1 Å shorter. Furthermore, a typical H · · · N hydrogen-bonding distance is typically slightly larger than 1.0 Å. From these comparisons and also from Stuart–Hershfelder models it is concluded that the hexacoordinated interstitial complexes are sterically tenable.