been isolated for short periods of time.[15] To determine whether the copper(II) complexes of *cis*-1,2-bis(dimethylarsino)ethylene would be stable, several reactions between copper(II) salts and *cis*-1,2-bis(dimethylarsino)ethylene were carried out, wherein the reaction of copper(II) perchlorate is typical. The copper(II) derivatives of *cis*-1,2-bis(dimethylarsino)ethylene are apparently even less stable than those of *o*-phenylenebis(dimethylarsine), since it proved impossible to isolate any copper(II) complexes, even for short periods of time. The copper(I) perchlorate prepared from this reaction is white and insoluble in all of the solvents with which it does not react, and consequently has not been further characterized.

Conclusions

Pure *cis*-1,2-bis(dimethylarsino)ethylene is an excellent bidentate chelating ligand. It readily forms complexes with the first-, second-, and third-row transition elements in both high and low oxidation states. The complexes of iron(II), iron(III), cobalt(III), and palladium(II) are remarkably stable. The metal derivatives of *cis*-1,2-bis(dimethylarsino)ethylene can be handled in the presence of air and water without appreciable decomposition. The iron complex $[Fe(\textit{cis}\text{-edas})_3][ClO_4]_3$ is particularly stable in contrast with $[Fe(das)_3][ClO_4]_3$ which decomposes on standing.

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(15) R. D. Feltham, unpublished results.

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Pentacoordinate Complexes. II.[1] The Electron Spin Resonance Spectrum of Pentakis(methyl isocyanide)cobalt(II) and a Comparison with Pentacyanocobaltate(II)

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The esr spectrum of $Co(CH_3NC)_5^{2+}$ in ethylene glycol–water glasses and solutions has been investigated in the temperature range 77–300°K. The *g* values observed are consistent with a square-pyramidal structure for this complex. Evidence is presented for increased unpaired electron delocalization in the $Co(CH_3NC)_5^{2+}$ ion in comparison with the pentacyano complex $Co(CN)_5^{3-}$; this may explain the difference in chemical reactivity of the two complexes. Optical spectra for $Co(CH_3NC)_5^{2+}$ are also reported.

Introduction

Pentacoordinated transition metal ions have been the subject of recent studies concerned with elucidating the molecular structure of these complexes in solution.[3-5] The two most likely geometries for such ions are the trigonal bipyramid and the square pyramid, of D_{3h} and C_{4v} symmetry, respectively.

Recently, Alexander and Gray[4] have shown that the optical and esr spectra of $Co(CN)_5^{3-}$ can be explained by assuming a square-pyramidal ground-state geometry for this complex. As part of a continuing study of pentacoordinated Co(II) ions,[1] we have investigated the physical properties of the low-spin pentakis(methyl isocyanide)cobalt(II) ion using optical and esr methods. The results of this study, which indicate that the symmetry of $Co(CH_3NC)_5^{2+}$ is also C_{4v}, provide the basis for some interesting comparisons of the physical and chemical properties of the two ions.

Experimental Section

Materials.—Baker Analyzed reagent grade chemicals were used. Methyl isocyanide was prepared according to the method of Casanova, *et al.*,[6] and redistilled twice to ensure purity. The uv spectrum of the product in water showed no band at 940 mμ which is characteristic for quinoline used in the synthesis. Gas chromatographic analysis of the methyl isocyanide also showed no trace of quinoline or acetonitrile. The preparation of $Co_2(CH_3NC)_{10}(NO_3)_4$ was accomplished by adding a small excess of CH_3NC to the cobaltous salt in absolute ethanol at 0° under nitrogen in the absence of light. The resultant red solid was washed with ethanol and used immediately or stored in Dry Ice.

Analysis.—Optical spectra of the complex in aqueous solution were recorded on a Cary Model 14 spectrophotometer to verify the purity of the sample. No evidence for the presence of quinoline was observed. Gas chromatographic analysis showed no trace of acetonitrile and thus ruled out the possibility of a Co(II)-catalyzed isomerization of CH_3NC to CH_3CN.

Esr Spectra.—A Varian V-4502 X-band esr spectrometer and 9-in. magnet equipped with Fieldial were employed. Field

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intensities were measured with a gaussmeter which was calibrated using DPPH attached to the outside of the sample tube. Samples of $\sim 10^{-4}$–10^{-6} M $Co(CH_3NC)_5^{2+}$ were prepared in deoxygenated ethylene glycol–water solutions and frozen in a quartz tube. Mixtures in a series of ratios from 2:3 up to 3:2 were tried; the esr spectra were not significantly different over this range of concentrations. Computed esr spectra were determined by the method of Ibers and Swalen[7] for an axial spin Hamiltonian with ^{59}Co ($I = {}^7/_2$) hyperfine structure. The rms deviations of the calculated spectra from those observed were 5.0 and 4.1 for the $Co(CH_3NC)_5^{2+}$ ion with and without excess CH_3NC present, respectively.

Results

Esr spectra of dilute mixtures of $Co(CH_3NC)_5^{2+}$ in ethylene glycol–water solutions and glasses were obtained over the temperature range 77–300°K both in the presence and in the absence of a slight excess of CH_3NC. In all cases, the spectra at 77°K consisted of an overlapping pattern of eight line shapes characteristic of an axial spin Hamiltonian[8] with a strong ^{59}Co hyperfine interaction.

Figure 1 shows the esr spectrum (I) of the isocyanide complex in a 40% ethylene glycol–water glass at 77°K. The assignment of such spectra has been discussed by many authors.[9] In the case of $Co(CH_3NC)_5^{2+}$, the spectrum is qualitatively similar to that of $Co(CN)_5^{3-}$ with $g_\perp > g_{||}$. The ^{59}Co hyperfine interaction produces a set of eight lines for each principal g value, with those belonging to $g_\perp$ being the more intense. Hence, in Figure 1, at least four of the lines belonging to $g_{||}$ are hidden under the perpendicular line shapes at higher field. One of the ^{59}Co lines is further split into a triplet with a separation of 5.2 G and approximately equal intensities.

The esr spectrum (II) of $Co(CH_3NC)_5^{2+}$ in 40% ethylene glycol–water at 77°K in the presence of a slight excess of CH_3NC is shown in Figure 2. The spectrum resembles that of the ion with no excess CH_3NC except that it is considerably less anisotropic, as is evidenced by the coalescing of several of the parallel and perpendicular lines. In this case, six of the lines belonging to $g_{||}$ are not observed. Under high gain, one of the observed parallel lines is also split; in this case the structure can be approximated by five lines separated by 5.2 G and relative intensities in the ratio 1:2:3:2:1.

Spectra I and II were assigned by making estimates of $g_{||}$, $g_\perp$, $A_{||}$, and $A_\perp$ from the observed spectra and then fitting the experimental line shape with a computed one calculated by the method of Ibers and Swalen.[7] The computed spectra are also shown in Figures 1 and 2. The resulting parameters are given in Table I. These were verified independently using a digital XY plot of the spectrum calculated using the axial program developed by Vänngard and Aasa.[10]

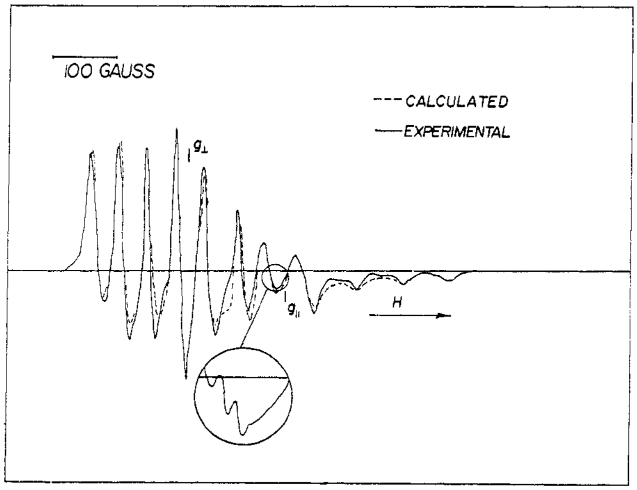

Figure 1.—The esr spectrum of $Co(CH_3NC)_5^{2+}$ in 40% ethylene glycol–water at 77°K. Excess CH_3NC is not present. The insert represents one of the parallel lines under high gain.

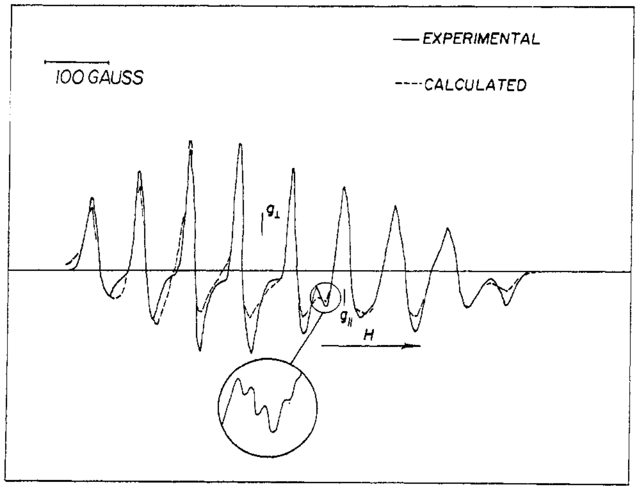

Figure 2.—The esr spectrum of $Co(CH_3NC)_5^{2+}$ in 40% ethylene glycol–water at 77°K. Slight excess CH_3NC is present. The insert represents one of the parallel lines under high gain.

TABLE I

ESR PARAMETERS FOR ISOCYANIDE AND CYANIDE[4] COMPLEXES OF COBALT(II)[a]

Complex	$g_{\parallel}$	$g_\perp$	$A_{\parallel}$, G	$A_\perp$, G	$\langle g\rangle_{calcd}$[b]	$\langle g\rangle_{exptl}$
I. $Co(CH_3NC)_5^{2+}$						
77°K	2.000 (2)	2.117 (1)	78 (1)	57 (1)	2.080 (2)	
300°K						2.01 (5)
II. $Co(CH_3NC)_5^{2+}$ Excess CH_3NC,						
77°K	2.025 (2)	2.092 (1)	65 (2)	75 (2)	2.070 (2)	
III. $Co(CN)_5^{3-}$						
77°K	1.992 (5)	2.157 (5)	87 (2)	28 (2)	2.102 (5)	
300°K						2.10 (1)

[a] Numbers in parentheses indicate uncertainty in last digit shown. [b] $\langle g\rangle = {}^1/_3(2g_\perp + g_{||})$.

Esr spectra of the complex were also obtained at 20° intervals from 77 to 273°K. Other than a loss of hyperfine structure and considerable line broadening, no unusual behavior was noted. Although $Co(CH_3NC)_5^{2+}$ is unstable in aqueous solution above 0°, spectra of the transient species were recorded at pH 5–6 and 20°. The spectrum was isotropic with $g \sim 2.01$.

The optical spectrum of $Co(CH_3NC)_5^{2+}$ in water solution at pH of 5–6 and at a pH of 7 was essentially the same as reported by Pratt and Silverman.[7] We

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[7] J. A. Ibers and J. D. Swalen, *Phys. Rev.*, **127**, 1914 (1962).

[8] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

[9] See, for example, R. Wilson and D. Kivelson, *ibid.*, **44**, 154 (1966).

[10] T. Vänngard and R. Aasa, Proceedings of the First International Conference on Paramagnetic Resonance, W. Low, Ed., Academic Press, New York, N. Y., 1963, p 509.

observed that the stability of the complex may be extended if the pH is lowered to approximately 6. An attempt was made to obtain the optical spectrum at 77°K but experimental difficulties prevented resolution of the bands.

The data obtained in these experiments are summarized in Tables I and II. For the purpose of later discussion we have listed the results obtained previously for $Co(CN)_5^{3-}$.[4]

Table II

Optical Spectra of Cyanide and Isocyanide Complexes

$Co(CN)_5^{3-}$ [4] Max, cm^{-1} (ϵ)	$Co(CH_3NC)_5^{2+}$ Max, cm^{-1} (ϵ)
10,350 (233)	14,280 (300)
16,200 (7)	22,200
23,300 (65)	30,300 (~10)
31,700 (527)	38,300
35,700 (4030)	
38,100 (980)	
43,300 (6500)	

Discussion

Esr Spectra.—Simple considerations of crystal field theory predict a ^2E_g ground state for the low-spin configuration of a d^7 ion in a field of octahedral symmetry. If an axial ligand is removed to form a pentacoordinated complex, the degeneracy of both the lower t_{2g} and upper e_g levels will be partially removed. In this situation, the ground-state configuration is either $(e)^4(b_2)^2(a_1)^1$ or $(e'')^4(e')^3$,[4] corresponding to C_{4v} or D_{3h} symmetry, respectively. That our results are consistent with C_{4v} symmetry for $Co(CH_3NC)_5^{2+}$ can be seen by a comparison of the predicted g values in the two cases.

In the case of C_{4v} symmetry, application of the method of Abragam and Pryce[11] yields the following expressions for the principal values of the g tensor, correct to first order

$$g_{\parallel} = g_e, \quad g_{\perp} = 2.002 + 6|\xi|/\Delta \qquad (1)$$

Here, ξ is the one-electron spin–orbit parameter, $g_e = 2.002$, and $\Delta = E(a_1) - E(e')$. For a $^2E'$ ground state in D_{3h} symmetry, $g_{\parallel} \gg g_e$.[4] Thus, by comparison of these predictions with the observed g values shown in Table I, the esr spectra of $Co(CH_3NC)_5^{2+}$ point to a structure of C_{4v} symmetry for this ion, as well as the pentacyano complex. The deviation of the measured $g_{\parallel}$ from g_e is presumably due to second-order effects not included in eq 1.

Using the measured value of $g_{\perp}$ in the absence of excess ligand (2.117) and $\xi \leqslant 540$ cm^{-1},[12] eq 1 yields for Δ the estimate $\Delta \leqslant 27{,}800$ cm^{-1}. This can be compared with the value $\Delta \leqslant 21{,}000$ cm^{-1} for $Co(CN)_5^{3-}$ obtained in a similar way from the published g values (see Table I).

In the presence of excess ligand, the esr spectrum of $Co(CH_3NC)_5^{2+}$ becomes less anisotropic; in this case, $\Delta \leqslant 36{,}000$ cm^{-1}. The decrease in $|g_{\perp} - g|$ is consistent with the view that, in the presence of excess CH_3NC, the complex is essentially hexacoordinate, but, because the spectrum is still anisotropic, the axial and equatorial metal–ligand bond distances must be unequal. The A-value anisotropy is also reduced by the addition of excess ligand. The observation that Δ increases as excess ligand is added suggests that the splitting of the upper a_1, b_1 levels in C_{4v} symmetry is greater than that of the lower e, b_2 levels. This result has also been observed in $Co(CN)_5^{3-}$.[4,13]

The additional splitting of one of the ^{59}Co hyperfine lines into an apparent triplet (and a quintet in the presence of excess ligand) can be interpreted as hyperfine structure which arises from a contact interaction with the ^{14}N nucleus ($I = 1$) of a CH_3NC ligand. The quintet pattern might be expected if the complex becomes six-coordinate on addition of excess ligand, although no structural evidence for a six-coordinated cobalt(II) cyanide complex has been reported.[14]

The possibility that this splitting can be explained by a ^{14}N hyperfine interaction is interesting in view of recent X-ray studies on $Co_2(CH_3NC)_{10}(ClO_4)_4$.[15] These have shown that the ligands in $Co_2(CH_3NC)_{10}(ClO_4)_4$ are bonded through the carbon atom to the central metal ion. Hayes[16] has recently observed ^{14}N hyperfine structure in the esr spectrum of $Mo(CN)_5NO^{3-}$ due to the nitrogen atoms of the carbon–metal bonded ligands. However, since the additional splitting in $Co(CH_3NC)_5^{2+}$ is observed on only one line of each spectrum and because the esr spectra are not well resolved, further work is necessary before our result can be fully interpreted.

Optical Spectra.—Pratt and coworkers[17] have concluded from a qualitative comparison of optical spectra that the pentakis(methyl isocyanide) and pentacyanide complexes of Co(II) are actually six-coordinate in water, $Co(CH_3NC)_5 \cdot H_2O^{2+}$ and $Co(CN)_5 \cdot H_2O^{3-}$, respectively. They have based their conclusion on the observation that the $Co(C_6H_5NC)_5^{2+}$ complex may exist in an aquated blue form which may be completely dehydrated to a yellow form. Since the uv spectrum of the aquated blue form is similar in many respects to the pentakis(methyl isocyanide) and pentacyanide complexes in solution, they reasoned that both of these complexes must be aquated as well. Although our current esr data are not sufficiently detailed enough to draw any conclusions with regard to the aquation of these complexes, Caulton[13] has shown that an analysis of the optical spectrum of the pentacyanide complex does not lead to any definite decision about the existence of $Co(CN)_5 \cdot H_2O^{3-}$. It appears that additional information is necessary before the question of aqua-

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tion in the pentakis(methyl isocyanide) and pentacyanide cobalt(II) complexes may be decided upon.

Chemical Behavior.—The complexes $Co(CN)_5^{3-}$ and $Co(CH_3NC)_5^{2+}$ offer some arresting physical and chemical comparisons as well. Green, high-pH, aqueous solutions of $Co(CN)_5^{3-}$ react readily with hydrogen,[18] oxygen,[19] and carbon monoxide[20] at room temperature and atmospheric pressure. The radical character of $Co(CN)_5^{3-}$ has been supported by product studies[21] with alkyl halides and kinetic[22] as well as polarographic[23] analysis of its many reactions. All of these contributions suggest that there is a ready availability of electron density on the central cobalt atom in $Co(CN)_5^{3-}$.

In contrast, the blue $Co(CH_3NC)_5^{2+}$ ion shows no evidence of reaction with carbon monoxide, hydrogen, oxygen, or methyl iodide. It does react with nucleophilic species and exhibits a chemistry reminiscent of $Co_2(CO)_8$.[24] Such dramatic differences in the chemical properties of the two ions suggest that there are important differences in their electronic and/or molecular structures.

While the investigations reported here on the esr and optical porperties of $Co(CH_3NC)_5^{2+}$ have uncovered no changes in the over-all symmetries of the ions, there do appear to be some subtle differences between the two complexes. In fact, most of these can be explained in terms of an increased delocalization of the unpaired electron over the ligand orbitals in the $Co(CH_3NC)_5^{2+}$ ion. Qualitatively, this might be expected in view of the negatively charged ligands in $Co(CN)_5^{3-}$, and this phenomenon may explain the increased chemical reactivity of the pentacyano complex.

Bowers and Owen[25] have discussed in qualitative terms some of the expected properties of an esr spectrum for an ion in which there is extensive delocalization. Among the indicators of such behavior are a reduction in g values, a reduction of the metal hyperfine interaction, and a ligand hyperfine interaction. Some of these phenomena have been observed in the esr spectra of $Co(CH_3NC)_5^{2+}$ reported here. Indeed, inspection of Table I reveals that the g value anisotropy of the methyl isocyanide complex is considerably reduced from that observed in $Co(CN)_5^{3-}$. This is consistent with more delocalization in the former situation.

The lack of information regarding the relative signs of $A_{\parallel}$ and $A_{\perp}$ for the two complexes precludes a determination of the change in the isotropic ^{59}Co coupling constant. Hence our data cannot be used as evidence for the reduction of the metal hyperfine interaction in $Co(CH_3NC)_5^{2+}$. However, it is interesting to note that the possible existence of ^{14}N hyperfine structure in the esr spectrum of this ion supports the concept of increased delocalization.

Although the extent of electron delocalization in ligands such as CO, CN^-, and CH_3NC has not been clearly defined, some additional remarks place our result in perspective with other work. The data obtained on $Co(CH_3NC)_5^{2+}$ can be explained by an increase in the π-acceptor tendency of the ligand relative to $Co(CN)_5^{3-}$. The isocyanide group as a ligand in transition metal complexes has been shown by Cotton and Zingales[26] to be formally isoelectronic with carbon monoxide. Thus the ligand may function as a σ-donor as well as a π-acceptor group.

Shriver and Posner[27] have discussed the effects of Lewis acids on transition metal cyanide adducts. In each case the complexation of H^+, BF_3, and CH_3^+ to CN^- leads to ligands which are better π acceptors and poorer σ donors than CN^-. Although the CH_3 group is generally regarded as an electron-releasing group,[28] this apparently does not radically affect the explanation that CH_3NC is a poorer σ donor than CN^-.

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