Contribution from the Centro di studio sulla Stabilità e Reattività dei composti di coordinazione, CNR,
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Reactivity of Cyanogen toward Compounds Containing Active Hydrogens at Carbon. 5. Cyanoimination Reaction of β-Keto Enolato and Schiff-Base Complexes of Copper and Nickel[§]

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Bis(β-keto enolato)copper(II) complexes and nickel(II) and copper(II) complexes of the Schiff-base condensation products of 1,3-diketones and diamines react with cyanogen in chlorinated solvents to give cyanoimino-substituted organometallic rings. The reactions occur with high yields and display rates that are strongly affected by the central metal and by the nature of the substituents on the ligands. The new compounds were fully characterized by elemental analysis, melting points, infrared and electronic spectroscopy, mass spectra, and thermoanalysis. The product [Cu(en(ba)$_2$(C$_2$N$_2$)$_2$)] (en(ba)$_2$ = Schiff base from benzoylacetone and ethylenediamine) was characterized by X-ray single-crystal analysis. The space group is $P2_1/n$, $Z = 4$, with cell parameters $a = 19.863$ (9) Å, $b = 12.184$ (8) Å, $c = 9.739$ (6) Å, and $\beta = 98.4$ (1)°.

In our previous papers of this series[1-5] we have reported on a new reaction mode of cyanogen which was found to react as an electrophile toward the Ni$_{1/2}$(acac) and Cu$_{1/2}$(acac)[6] rings undergoing insertion into the C–H methino bond.

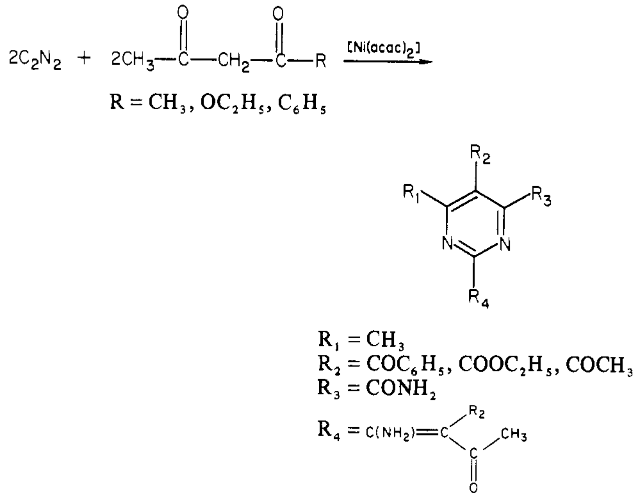
This reaction finds a straightforward application in the new one-pot synthesis of fairly sophisticated pyrimidines from[2,7] C_2N_2 and some β-dicarbonyls according to Scheme I.

In order to clarify the more inorganic aspects of this novel area of the chemistry of cyanogen, we have tested the reactivity of cyanogen with [Cu(eaa)$_2$] (eaa = ethyl acetoacetate), [Cu(ba)$_2$] (ba = benzoylacetonate), [Cu(dbm)$_2$] (dbm = dibenzoylmethanate), [Cu(tfacac)$_2$] (tfacac = trifluoroacetylacetonate), [Cu(en(acac)$_2$)], [Cu(en(ba)$_2$)], [Ni(en(acac)$_2$)], [Ni(en(ba)$_2$)], [Cu(pap)Cl], and [Ni(pap)Cl] (see Chart I).

The behavior of the chosen metal substrates toward cyanogen was expected to give information on the effect of the substituents on the reactivity of the C–H methino bond in the copper–1,3-diketonate skeleton and to reveal whether this remarkable insertion of C_2N_2 into the methino bond could be extended to related systems.

In spite of the vast amount of data available on the chemistry of Schiff-base complexes,[8] very little is known on the reactivity of the methino bonds that are present in the compounds derived from 1,3-diketones and diamines.[9,10] This fact did not make obvious the expectation of a similarity between the reactivity of C–H methino bonds present in rings as sketched in Chart I and those present in β-keto enolate metal complexes.

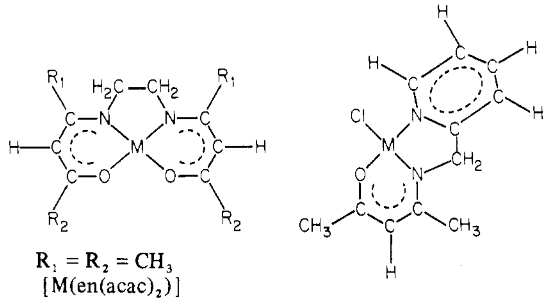
Scheme I



R = CH$_3$, OC$_2$H$_5$, C$_6$H$_5$

R$_1$ = CH$_3$
R$_2$ = COC$_6$H$_5$, COOC$_2$H$_5$, COCH$_3$
R$_3$ = CONH$_2$

Chart I



R$_1$ = R$_2$ = CH$_3$
[M(en(acac)$_2$)]
R$_1$ = CH$_3$, R$_2$ = C$_6$H$_5$
[M(en(ba)$_2$)]

[M(pap)Cl]

Experimental Section

The metal complexes used were prepared and purified according to the literature.[11-13] Solvents were reagent grade and were dried by conventional procedures, and technical grade cyanogen was purchased from Matheson, Belgium. Conveniently concentrated solutions of cyanogen were prepared by direct transfer of suitable amounts of gas from the cylinder into the desired volume of solvent. The C_2N_2 concentration was determined as previously described.[14]

Instruments and Spectral Data. Routine IR spectra were recorded on a Perkin-Elmer 457 instrument and electronic spectra on a Perkin-Elmer A72 instrument. The data are given in cm^{-1}, with ϵ values in cm^{-1} mol^{-1} dm^3.

Magnetic susceptibilities were determined at room temperature on a Gouy apparatus employing a Bruker B-M 6 magnet coupled with a Sartorius electrobalance. Mass spectra, thermogravimetric data, and elemental analysis were performed at the Inorganic Chemistry

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[§] Part of this work has been carried out during a stay of B.C. as Guest Professor at the Munich Polytechnic Institute of Inorganic Chemistry as an A. von Humboldt fellow.

(1) Corain, B.; Del Pra, A.; Filira, F.; Zanotti, G. *Inorg. Chem.* **1979**, *18*, 3523.

(2) Corain, B.; Crotti, C.; Del Pra, A.; Filira, F.; Zanotti, G. *Inorg. Chem.* **1981**, *20*, 2044.

(3) Corain, B.; Basato, M.; Visentin, G.; Zanotti, G., accepted for publication in *J. Chem. Soc., Dalton Trans.*

(4) Corain, B.; Basato, M.; Marcomini, A.; Klein, H. F. *Inorg. Chim. Acta* **1983**, *74*, 1.

(5) Corain, B.; Basato, M. *J. Organomet. Chem.* **1982**, *232*, C59.

(6) Corain, B.; Basato, M.; Warsame, A. *Chim. Ind.* (*Milan*) **1979**, *61*, 567. For a complete review see: Corain, B. *Coord. Chem. Rev.* **1982**, *47*, 165.

(7) Corain, B.; Basato, M.; Klein, H. F. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 972.

(8) Holm, R. H.; Everett, G. W., Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83.

(9) Howells, P. N.; Kenney, J. W.; Nelson, J. H.; Henry, R. A. *Inorg. Chem.* **1976**, **15**, 124.

0020-1669/83/1322-2744$01.50/0

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Cyanation of the Substrates. Typically, 1–3 mmol of the metallic reagents were added to 50 mL of dichloroethane or toluene containing an excess of C_2N_2 (generally a fivefold excess at room temperature) and moderately stirred for a time that varied between 3 min and 6 days, depending on the compound.

The products were, as a rule, dried in vacuo by mechanical pumping. The absence of reactivity exhibited by [Cu(tfacac)$_2$] and [Pd(pap)Cl] in $C_2H_4Cl_2$ and in toluene was checked by spectrophotometric tests (Cu^{II}) and by the recovery of the reagent (Pd^{II}). Reaction of C_2N_2 with the Schiff-base complexes was carried out in anhydrous solvents.

Preparation of the [Cu(β-keto enolato-C_2N_2)$_2$] Complexes. See Table III for UV–vis data.

[Cu(eaaC$_2$N$_2$)$_2$]. [Cu(eaa)$_2$] (1.2 mmol) was dissolved in 12 mL of $C_2H_4Cl_2$ containing ~0.30 M C_2N_2. After 3–4 min the product precipitated as gray needles, which were recrystallized from $C_2H_4Cl_2$: yield 72%; mp 174 °C; mass spectrum (*m/e*, relative intensity) 425.3 (molecular peak, theoretical 425.0) (0.14), 380.1 (0.19), 352.1 (0.13), 310.2 (0.69), 245.2 (0.47), 167.10 (1.00), 138.9 (0.91), 94.8 (0.95), 68.0 (0.82).

[Cu(baC$_2$N$_2$)$_2$]. [Cu(ba)$_2$] (1.0 mmol) was dissolved in 12 mL of $C_2H_4Cl_2$ containing ~0.30 M C_2N_2. After 1 h a gray-green solid began to separate. The filtration after 20 h gave the crude product (94%). Recrystallization from $C_2H_4C_2$ afforded the pure compound (yield 36%). The product decomposes at ca. 207 °C. Mass spectrum (*m/e*, relative intensity): 489.1 (molecular peak, theoretical 489.0) (0.006), 277.1 (0.02), 250.0 (0.02), 213.0 (0.31), 187.1 (0.35), 104.9 (1.00), 77.1 (0.64), 51.3 (0.29).

[Cu(dbmC$_2$N$_2$)$_2$]. [Cu(dbm)$_2$] (0.8 mmol) was suspended in 12 mL of $C_2H_4Cl_2$ containing 0.22 M C_2N_2. The suspension was left 2 days with vigorous stirring, and the crude green product was obtained in high yield (84%). The product was recrystallized from acetone (yield 24%). It decomposes at ca. 225 °C. Mass spectrum (*m/e*, relative intensity): 612.9 (molecular peak, theoretical 613.0) (0.001), 586.1 (0.001), 337.0 (0.006), 213.1 (0.14), 186.0 (0.26), 105.0 (1.00), 77.0 (0.67), 51.3 (0.43).

Preparation of the Metal–Schiff-Base–Cyanogen Complexes. [Cu(en(acac)$_2$(C$_2$N$_2$)$_2$)]. [Cu(en(acac)$_2$)] (5.00 mmol) was dissolved in 50 mL of $C_2H_4Cl_2$ containing ~0.6 M C_2N_2. After a few minutes a light green precipitate began to separate, and after 15 min the filtration yielded the pure product: yield 93%; mp 200–202 °C dec; UV 42 500 (ϵ = 23 000), 32 800 (ϵ = 22 000), 27 800 (ϵ = 14 000); vis 16 000 (ϵ = 150).

[Cu(en(ba)$_2$(C$_2$N$_2$)$_2$)]. [Cu(en(ba)$_2$)] (0.8 mmol) was suspended in 10 mL of $C_2H_4Cl_2$ containing ~0.6 M C_2N_2 with vigorous stirring. After 10 min a dark brown solution was obtained, after which the solution was left undisturbed for 24 h. By this procedure a 79% yield of dark green crystals, which are suitable for X-ray single-crystal analysis, can be obtained. The crystals must be washed with ethyl ether and dried in vacuo: mp 224–226 °C dec; UV 40 000 (ϵ = 37 000), 30 700 (sh), 28 200 (ϵ = 18 000); Vis 16 000 (ϵ = 180).

[Ni(en(acac)$_2$)] + C$_2$N$_2$. [Ni(en(acac)$_2$)] (1 mmol) was dissolved in 5 mL of dichloroethane containing ~0.4 M C_2N_2. The dark red solution so obtained was monitored for 120 h by IR spectra. Then the solvent was removed under reduced pressure; however, the remaining red-brown product exhibited elemental analyses that did not agree with any rational formulation. In contrast with this, IR analysis of the reactant solution showed a clean accumulation of a strong ν_{N-H} band at 3350 cm^{-1}, the intensity of which became constant after 120 h.

[Ni(en(ba)$_2$)] + C$_2$N$_2$. [Ni(en(ba)$_2$)] (1 mmol) was placed in a 50-mL stainless-steel autoclave and dissolved in 10 mL of $C_2H_4Cl_2$ containing 0.63 M C_2N_2. The reaction was carried out at 60 °C for 6 days without stirring. The red-brown suspension obtained after this time was filtered, and the red-brown precipitate gave the following analysis: Anal. Calcd for [Ni(en(ba)$_2$(C$_2$N$_2$)$_2$)]: C, 61.33; H, 4.35; N, 16.50. Found: C, 62.24; H, 4.75; N, 14.07; IR (Nujol): 3300 (N–H) 2200 (C≡N), 1630 (C=N).

Table I. Crystal Data for $CuC_{26}H_{22}O_2N_2$

M_r = 458.0
a = 19.863 (9) Å
b = 12.184 (8) Å
c = 9.739 (6) Å
β = 98.4 (1)°
V = 2332 Å^3
λ(Mo Kα) = 0.7107 Å
space group $P2_1/n$
Z = 4
F(000) = 1052 e

[Cu(papC$_2$N$_2$)Cl]. [Cu(pap)Cl] (1 mmol) was suspended in 10 mL of a 0.5 M C_2N_2 solution in $C_2H_4Cl_2$. The green suspension so obtained was vigorously stirred for 35 min and then filtered and washed with 10 mL of $C_2H_4Cl_2$. The yield was 77% of pure compound: mp 193–195 °C dec; UV 44 400 (ϵ = 16 000), 38 500 (ϵ = 12 500), 33 900 (ϵ = 11 000), 27 000 (ϵ = 6500); vis 23 500 (sh), 15 300 (ϵ = 100); mass spectrum (*m/e*, relative intensity) 339.0 (molecular peak, theoretical 339.0) (1.0), 289 (0.04), 287 (0.05).

[Ni(papC$_2$N$_2$)Cl] (Reaction in C$_2$H$_4$Cl$_2$). [Ni(pap)Cl] (0.7 mmol) was suspended in 10 mL of $C_2H_4Cl_2$ containing ~0.5 M C_2N_2. The suspension was vigorously stirred for 30 min and then filtered and washed with 30 mL of $C_2H_4Cl_2$. The yield was 76%. The greenish yellow product melts with decomposition at 252–254 °C. The elemental analysis fits reasonably well with the composition [Ni(papC$_2$N$_2$)Cl] (Anal. Calcd: C, 46.55; H, 3.91; N, 16.70. Found: C, 45.73; H, 3.98; N, 15.75). The IR spectrum in Nujol exhibits two N–H bands at 3370 and 3300 cm^{-1} (comparable intensity).

[Ni(papC$_2$N$_2$)Cl] = (Ni(pap)α). [Ni(pap)Cl] (0.35 mmol) was suspended in 10 mL of water-saturated toluene, which was 0.6 M in C_2N_2. The pale red suspension turned gradually to greenish yellow and was vigorously stirred for 6 days. Filtration yielded pure product as green-yellow microcrystalline powder. The yield was 92%. UV: 42 500 (ϵ = 24 500), 34 500 (ϵ = 12 000), 29 800 (ϵ = 9500). Vis: 24 100 (ϵ = 1500), 23 200 and 17 400 (very weak shoulders). Mass spectrum (*m/e*, relative intensity): 334.1 (molecular peak, theoretical 334.0) (0.04), 298.1 (0.09), 243.1 (0.33), 200.3 (0.11), 167.3 (0.18), 149.1 (0.46), 133.0 (0.35), 107.2 (0.64), 91.9 (0.95), 79.1 (1.00), 71.1 (0.28), 65.1 (0.45), 59.1 (0.47), 57.3 (0.45).

[Ni(papC$_2$N$_2$)Cl] = (Ni(pap)β). The reaction was carried out as described above, but in anhydrous toluene. The yield was 76% of a very pure green-yellow product melting at 259–260 °C dec. When this reaction was stopped after 24 h and the solid material filtered under argon, the IR spectrum in Nujol showed that it was largely [Ni(pap)Cl] but a weak and well-defined band at 3370 cm^{-1} indicated the presence of the (Ni(pap)α) species. UV: 42 500 (ϵ = 22 500), 34 500 (ϵ = 13 000), 29 800 (ϵ = 10 000), Vis: 24 100 (ϵ = 2500), 23 200 and 17 400 (very weak shoulders). Mass spectrum (*m/e*, relative intensity: 334.3 (molecular peak, theoretical 334.0) (0.02), 243.2 (0.04), 182.1 (0.06), 152.0 (0.21), 125.0 (0.29), 94.9 (0.41), 82.9 (0.20), 68.1 (0.27), 58.2 (1.00).

X-ray Structure Analysis of [Cu(en(ba)$_2$(C$_2$N$_2$)$_2$)]. Crystals of [Cu(en(ba)$_2$(C$_2$N$_2$)$_2$)] were obtained by direct precipitation from a solution containing originally 0.34 g of [Cu(en(ba)$_2$)] in 50 mL of $C_2H_4Cl_2$ 0.6 M in C_2N_2. After 24 h at 20 °C dark green crystals precipitated spontaneously.

The crystal parameters obtained by single-crystal diffractometry are given in Table I. X-ray data were collected from a crystal approximately 0.25 × 0.20 × 0.15 mm on a Philips PW 1100 four-circle diffractometer operating in the $\vartheta/2\vartheta$ scan mode (scan width 1.2°, scan speed 0.030° s^{-1}), with Mo Kα radiation monochromatized by a graphite crystal. A total of 4360 independent reflections up to ϑ = 25° were measured, of which 2272 had intensities greater than $2.5\sigma(I)$. During the data collection two standard reflections were measured every 180 min to check the stability of the crystal and the electronics. Intensities were corrected for Lorentz and polarization effects. Absorption and extinction corrections were ignored.

The position of the Cu atom was determined by the Patterson method, and the subsequent Fourier map showed the remainder of the molecule. Refinement of the structure was carried out by full-matrix least-squares analysis. In the last cycles of refinement the Cu, O, and N atoms were allowed to vibrate anisotropically and the H atoms introduced in calculated positions but not refined. The final R value for all the observed reflections was 0.081 (R_w = 0.069). The quantity minimized was $\sum w(|F_o| - |F_c|)$, where $w = 3.6/[\sigma^2(F) + 0.0001(F)^2]$. The correction for the real and imaginary part of the anomalous dispersion was applied for the Cu atom only. The scattering factors for all the atoms were taken from ref 15. All the calculations

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(10) Nagahara, T.; Kasuga, K.; Yamamoto, Y. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 235.

(11) McCarthy, P. J.; Hovey, R. J.; Ueno, K.; Martell, A. E. *J. Am. Chem. Soc.* **1955**, *77*, 5820.

(12) Uhlig, E.; Gottschling, E. *Z. Anorg. Allg. Chem.* **1970**, *376*, 113.

(13) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. "The Chemistry of β-Diketone Complexes and Allied Derivatives"; Academic Press: London, 1978.

(14) Corain, B.; Basato, M.; Bontempelli, G. *Anal. Chem.* **1981**, *53*, 124.

Table II. Analysis and Some Physical Properties of the Complexes $[M((lig)C_2N_2)_2]$ and $[M((lig)C_2N_2)Cl]$

complex	% calcd C	% calcd H	% calcd N	% calcd Cl	% found C	% found H	% found N	% found Cl	IR data (Nujol), cm^{-1} ν_{N-H}	$\nu_{C\equiv N}$	$\nu_{C=N}$	μ, μ_B
$[Cu(eaaC_2N_2)_2]$	45.13	4.22	13.15		45.25	4.18	13.00		3280 (ms)	nd[a]	1710 (ms)	2.63
$[Cu(baC_2N_2)_2]$	58.85	3.67	11.43		58.92	3.62	11.30		3320 (ms)	nd	1627 (ms)	2.08
$[Cu(dbmC_2N_2)_2]$	66.51	3.58	9.12		66.18	3.63	9.40		3253 (ms)	nd	1629 (ms)	2.34
$[Cu(acacC_2N_2)_2]$	45.96	3.85	15.31		45.78	3.94	14.91		3271 (ms)	2225 (w)	1635 (ms)	2.03
$[Cu(en(acac)_2(C_2N_2)_2)]$	49.29	4.65	21.55		49.49	4.51	21.57		3280 (ms)	2220 (w)	1650 (ms)	1.88
$[Cu(en(ba)_2(C_2N_2)_2)]$	60.75	4.31	16.35		60.07	4.30	16.08		3315 (ms)	2220 (w)	1645 (ms)	2.02
$[Cu(papC_2N_2)Cl]$	45.89	3.85	16.47	10.42	46.44	4.02	16.15	10.55	3285 (ms)	2230 (w)	1675 (ms)	1.91
α-$[Ni(papC_2N_2)Cl]$	46.55	3.91	16.70	10.57	44.75	3.78	17.19	10.47	3370 (ms)	2235 (w)	1665 (ms)	
β-$[Ni(papC_2N_2)Cl]$	46.55	3.91	16.70	10.57	46.40	4.09	16.80	10.79	3300 (ms)	2240 (w)	1670 (ms)	

[a] Not detectable.

were performed by using the SHELX programs[16] on the IBM 370/158 of the Computing Centre of the University of Padua.

Results and Discussion

General Remarks. All the complexes employed except $[Cu(tfacac)_2]$ and $[Pd(pap)Cl]$ react with C_2N_2 at ambient conditions or at moderate temperature (60 °C for $[Ni(en(ba)_2)]$.

In agreement with the findings of Nelson[9] and co-workers concerning the reactivity of $[M(en(ba)_2)]$ (M = Ni, Cu) with reactive isocyanates, Ni^{II} Schiff-base complexes react slower than the Cu^{II} complexes. The reactivity of these latter complexes is rather comparable with that exhibited by the Cu^{II} β-keto enolato complexes investigated here, for which the reaction rate in $C_2H_4Cl_2$, estimated from preparative and spectroscopic evidence, is in the order

$$[Cu(eaa)_2] > [Cu(acac)_2] \gg [Cu(ba)_2] \simeq [Cu(dbm)_2]$$

The reaction yields were very high, and the crude products were obtained almost analytically pure. It is remarkable that, in contrast with what was observed in the behavior of the primary cyanogen addition product from $[Ni(acac)_2]$, no isomerization of the crude product was observed upon recrystallization[1] and the IR spectra of the crude and recrystallized species are practically identical.

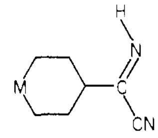
The tetradentate Schiff-base Cu^{II} complexes react in $C_2H_4Cl_2$ with C_2N_2 within minutes ($[Cu(en(acac)_2)]$) or hours ($[Cu(en(ba)_2)]$) to give the corresponding addition–insertion products in high yields. $[Ni(en(acac)_2)]$ requires days, at room temperature, to react completely (spectrophotometric evidences given by IR spectra in solution), while $[Ni(en(ba)_2)]$ has to be treated at 60 °C in an autoclave for 6 days to give an incomplete addition of C_2N_2 to the substrate.

The Schiff-base complexes $[Ni(pap)Cl]$ and $[Cu(pap)Cl]$ react in $C_2H_4Cl_2$ to give addition compounds in high yields. $[Cu(pap)Cl]$ gives rapidly (reaction complete in less than 1 h) only one kind of product, analytically pure, which cannot be transformed into any isomeric species upon thermal treatment. $[Ni(pap)Cl]$ gives, in contrast, a mixture of two species in $C_2H_4Cl_2$ (shown by analysis to be $[Ni(papC_2N_2)Cl]$), while the individual components, both shown by analysis to be $[Ni(papC_2N_2)Cl]$, can be obtained in water-saturated or anhydrous toluene as reaction media. The first was indicated as the α and the second as the β species. Both reactions take 6 days to go to completion.

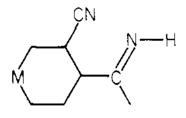
Finally, by monitoring of the IR spectra of the solid present when suspensions of $[Ni(pap)Cl]$ in anhydrous toluene were reacted with excess C_2N_2, it was observed that after 1 day the solid contained almost pure $[Ni(pap)Cl]$ and traces of the α compound exhibiting a ν_{N-H} band at 3370 cm^{-1}.

The scope of the isolated products and their analytical IR, UV, and magnetic data are reported in Table II.

The elemental composition of the isolated products clearly indicates that each reacting complex coordinates one C_2N_2 molecule per β-keto enolate–metal or β-keto iminate–metal ring. The IR data shows that a cyanoimination reaction has occurred, i.e. the formation of C≡N and C=N—H groups in the "organometallic" rings upon C_2N_2 insertion into the C–H methino bonds. In the cases of $[Cu(eaa)_2]$, $[Cu(ba)_2]$, and $[Cu(dbm)_2]$ the products do not exhibit any detectable C≡N band, but there are spectroscopic explanations for such an unappreciable intensity.[17] The IR data, on the whole, show that the following schematic molecular frameworks should be present in the cyanoimino-1,3-diketo enolate and cyanoimino–keto iminate complexes:



$M\alpha_2$



$M\beta_2$

The formation of these kinds of chemical frameworks, i.e. the occurrence of cyanoimination of the organometallic ring, appears to be a feature of all but two of the substrates used. Thus, only $[Pd(pap)Cl]$ and $[Cu(tfacac)_2]$ are inactive toward C_2N_2, while $[Ni(en(acac)_2)]$ and $[Ni(en(ba)_2)]$, which do not lead to the isolation of pure dicyanogen addition compounds, offer very good spectroscopic evidence for the occurrence of cyanoimination of the organometallic rings.

As to the nature of the $[M((ligand)C_2N_2)]$ species, we have already found that the cyanation of $[Cu(acac)_2]$ gives a $Cu\beta_2$ species.[3] For $[Ni(acac)_2]$ the preliminary formation of a $Ni\alpha_2$ complex (which evolves into $Ni\beta_2$) has been proposed[1] even though unambiguous proof of the real nature of $Ni\alpha_2$ is not yet available and specific work is in progress in this connection.[18]

On the basis of the ascertained β-nature of the stable complexes derived from $[Ni(acac)_2]$ and $[Cu(acac)_2]$, and of the β-nature of the compound $[Cu(en(ba)_2(C_2N_2)_2)]$ (see below), we propose a β-nature for the compounds $[Cu(eaaC_2N_2)_2]$, $[Cu(baC_2N_2)_2]$, and $[Cu(dbmC_2N_2)_2]$. In the case of $[Cu(eaaC_2N_2)_2]$ and of $[Cu(baC_2N_2)_2]$ (which are "asymmetric" β-dicarbonyl species) two isomeric β species are, of course, conceivable, but no reasonable choice in this connection appears to be possible to date. The same problem concerns the ligand geometry (vide infra) in all the other products of the action of C_2N_2 on the Schiff-base complexes we have investigated, and the relevant proposals are outlined below.

Spectroscopic and Magnetic Data. Spectral data in the UV–vis range for $[Cu(ligC_2N_2)_2]$ (lig = ligand) and for the

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(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.
(16) Sheldrick, G. "SHELX-76 System of Computing Programs"; University of Cambridge: Cambridge, England, 1976.
(17) Bellamy, L. J. "The Infrared Spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, 1975; Vol. 1, p 297.
(18) Ballotta, C.; Corain, B., work in progress.

Table III. Spectral Data in the UV-vis Range for $[Cu((\beta\text{-keto enolate})C_2N_2)_2]$ Complexes Compared with Those of the Parent Compounds in CH_2Cl_2

complex	λ_{max}, cm^{-1}				
	band I[b]	band II[b]	band III[b]	band IV[b]	band V[c]
$[Cu(acac)_2]$	40 500	33 600	31 500	18 200	15 400
$[Cu\beta_2]$	37 000	34 800	29 000	not obsd	17 400
$[Cu(eaa)_2]$	38 500	36 000	not obsd	16 700	14 300
$[Cu(eaaC_2N_2)_2]$	40 300 (19)	33 900 (17)	29 600 (13.8)	not obsd	17 000 (73)
$[Cu(ba)_2]$	38 500	~33 000[a]	38 800	18 500	15 100
$[Cu(baC_2N_2)_2]$	39 200 (28.3)	33 000 (25.1)	29 000 (15.2)	~20 400[a]	17 000 (102)
$[Cu(dbm)_2]$	37 300	35 100	28 300	18 200	15 100
$[Cu(dbmC_2N_2)_2]$	38 200 (20.2)	33 000 (22.8)	28 200 (19.3)	~20 000[a]	16 700 (114)

[a] Just detectable shoulder. [b] ϵ ($\times 10^{-3}$ cm^{-1} mol^{-1} dm^{-3}) in parentheses. [c] ϵ (cm^{-1} mol^{-1} dm^{3}) in parentheses.

$[Cu(lig)_2]$ species are reported in Table III.

The combination of the spectroscopic data in the visible range with the magnetic moments of the Cu^{II} complexes indicates that the square-planar monomeric geometry of the starting materials[11-13] is maintained in the cyanoimino derivatives.

The spectral findings in the UV–vis range and the observed μ data (μ_B) (2.03 $[Cu\beta_2]$; 2.08, $[Cu(baC_2N_2)_2]$; 2.63, $[Cu(eaaC_2N_2)_2]$; 2.34, $[Cu(dbmC_2N_2)_2]$) suggest some considerations. The addition of cyanogen to the C–H methino bond does not cause remarkable changes in the shape of the spectra and position of the bands of the reacting complexes, thus indicating an overall maintenance of the geometry of the $[CuO_4]$ chromophore. The effect of the cyanoimination on the UV absorptions of the β-keto enolate ring is erratic, but an appreciable bathochromic effect is observed for band III. The concomitant ipsochromic trend of bands IV and V may explain the lack of band IV for $[Cu\beta_2]$ and $[Cu(eaaC_2N_2)_2]$.

The ipsochromic effect observed for band V indicates that the cyanoimination of the β-keto enolato ligands produces an appreciable increase of the corresponding ligand field strength, which can be evaluated roughly as around 15%. This finding is reasonable and expected if one remembers that the cyanoimination of the Ni-bonded $acac^-$ ligand causes a dramatic destabilization of the trimeric octahedral structure of $[Ni(acac)_2]$ in favor of the square-planar monomeric structure,[1] which should be due to the increase of the covalent nature of the Ni–O bond.[19]

This kind of electronic effect was not observed, in general, when C_2N_2 causes cyanoimination of metal-bonded Schiff bases.

Thus (see Table IV) the cyanoimination of $[Cu(en(acac)_2)]$ and of $[Cu(en(ba)_2)]$ produces a clear bathochromic shift in the visible range. Again an ipsochromic effect is observed in going from $[Ni(pap)Cl]$ to $[Ni(papC_2N_2)Cl]$, while contradictory figures are obtained for $[Cu(papC_2N_2)Cl]$.

The UV–vis spectrum of $[Cu(papC_2N_2)Cl]$ is not so similar, on the whole, to that of the parent compound in demonstrating the square-planar nature of the moiety $[CuON_2Cl]$ in the product. However, this structure is strongly suggested (see below) by the X-ray Debye spectrum of $[Cu(papC_2N_2)Cl]$ compared to that of β-$[Ni(papC_2N_2)Cl]$. For this compound and for its α-isomer, the square-planar nature is warranted by the 24 100-cm^{-1} band, which is typical of a Ni^{II} square-planar complex in a medium ligand field environment.

The square-planar geometry of the $[CuN_2O_2]$ moieties in $[Cu(en(ba)_2(C_2N_2)_2)]$ and $[Cu(en(acac)_2(C_2N_2)_2)]$ is ascertained by the X-ray data for the first complex and by the close analogy of their visible spectra for the second complex.

The magnetic moments for the Cu^{II} compounds look fairly normal[20] and clearly indicate the absence of any Cu^{II}–Cu^{II} interaction between adjacent $[CuO_4]$, $[CuN_2O_2]$, or $[CuN_2OCl]$ moieties in the solid state.

Table IV. Spectral Data in the Visible Range for the $[M((\text{Schiff base})C_2N_2)]$ Complexes Compared with Those of the Parent Compounds

complex	λ_{max}, cm^{-1}	
	band I	band II
$[Cu(en(acac)_2)]$	18 300	~15 400[a]
$[Cu(en(acac)_2(C_2N_2)_2)]$	16 000	not obsd up to 11 000
$[Cu(en(ba)_2)]$	18 200	~15 400[a]
$[Cu(en(ba)_2(C_2N_2)_2)]$	16 000	not obsd up to 11 000
$[Cu(pap)Cl]$	22 500	15 900
$[Cu(papC_2N_2)Cl]$	23 500	15 300
$[Ni(pap)Cl]$	19 600	
α-$[Ni(papC_2N_2)Cl]$	24 100	
β-$[Ni(papC_2N_2)Cl]$	24 100	

[a] Barely detectable shoulder.

Thermal, Mass, and X-ray Powder Data. The cyanoimino keto enolato copper(II) complexes are species that exhibit, in general, less thermal stability than the parent compounds. Their vapor pressures change irregularly with respect to the corresponding parent complexes. Thus, $[Cu\beta_2]$ and $[Cu(acac)_2]$ have quite similar volatilities, while this feature decreases on going from $[Cu(eaa)_2]$ to $[Cu(eaaC_2N_2)_2]$. Again $[Cu(ba)_2]$ and $[Cu(baC_2N_2)_2]$ display similar vapor pressure profiles, while for $[Cu(dbm)_2]$ an appreciable increase of volatility occurs upon cyanogen addition. These data offered useful indications for the choice of the best conditions for mass spectral analysis. In all cases the molecular peak could be clearly detected and a perfect agreement between the calculated and observed mass figures was observed. $[Cu\beta_2]$ and $[Cu(eaaC_2N_2)_2]$ exhibited considerable stability of the molecular ion while $[Cu(baC_2N_2)_2]$ and $[Cu(dbmC_2N_2)_2]$ showed poor molecular stability under the conditions tested.

The Schiff-base derivatives were not as thoroughly investigated by thermal and mass spectral methods. Only the pap derivatives were investigated by the mass spectrometer, and $[Cu(papC_2N_2)Cl]$ required the "field ionization" technique. The mass spectra of the products denoted as α- and β-$[Ni(papC_2N_2)Cl]$ gave the expected molecular ion peak but quite different fragmentation patterns.

The complex $[Cu(papC_2N_2)Cl]$ and the α and β forms of $[Ni(papC_2N_2)Cl]$ were carefully compared in terms of X-ray Debye spectra. Those of Cu^{II} and of the β form of Ni^{II} were similar to each other and quite different from that of the α-Ni^{II} complex.

Structural Considerations. As suggested above, the $[Cu((\beta\text{-keto enolato})C_2N_2)_2]$ complexes can reasonably be proposed to be β-type species by analogy with $[Cu\beta_2]$.

$[Cu(en(ba)_2(C_2N_2)_2)]$ exhibits a β structure as shown in Figure 1.

The X-ray structure analysis of $[Cu(en(ba)_2(C_2N_2)_2)]$ showed unambiguously that the compound is the (3,10-bis(cyanocarbonyl)-4,9-dimethyl-2,11-diphenyl-1,5,8,12-tetraa-

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(19) Addison, A. W.; Graddon, D. P. *Aust. J. Chem.* **1968**, *21*, 2003.

(20) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; p 814.

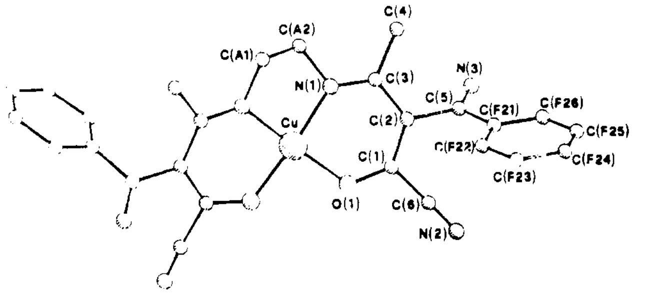

Figure 1. X-ray structure of $[Cu(en(ba)_2(C_2N_2)_2)]$.

Table V. Final Positional Parameters (with Esd's in Parentheses) for Non-Hydrogen Atoms

	x/*a*	*y*/*b*	*z*/*c*
Cu	0.10884 (5)	0.1795 (1)	0.3683 (1)
O(1)	0.1861 (4)	0.1283 (7)	0.2831 (5)
O(11)	0.0488 (3)	0.0755 (6)	0.2627 (8)
N(1)	0.1618 (3)	0.2997 (6)	0.4612 (7)
N(11)	0.0367 (3)	0.2238 (6)	0.4748 (7)
N(2)	0.3410 (4)	0.0620 (8)	0.2044 (10)
N(3)	0.3625 (3)	0.3743 (5)	0.3612 (7)
N(21)	−0.0740 (4)	−0.0626 (7)	0.0730 (9)
N(31)	0.1323 (3)	0.0442 (4)	0.6400 (7)
C(1)	0.2489 (4)	0.1677 (8)	0.3149 (9)
C(2)	0.2709 (4)	0.2584 (7)	0.3978 (9)
C(3)	0.2255 (4)	0.3258 (8)	0.4628 (9)
C(4)	0.2562 (5)	0.4259 (8)	0.5456 (10)
C(5)	0.3453 (4)	0.2900 (7)	0.4108 (9)
C(6)	0.3014 (5)	0.1094 (8)	0.2522 (10)
C(A1)	0.0653 (4)	0.3011 (7)	0.5851 (10)
C(A2)	0.1178 (5)	0.3699 (8)	0.5295 (10)
C(11)	−0.0148 (4)	0.0555 (7)	0.2769 (9)
C(21)	−0.0509 (4)	0.0989 (7)	0.3800 (9)
C(31)	−0.0221 (4)	0.1767 (7)	0.4812 (8)
C(41)	−0.0589 (4)	0.2013 (8)	0.6032 (9)
C(51)	−0.1201 (4)	0.0508 (7)	0.3811 (9)
C(61)	−0.0515 (4)	−0.0140 (8)	0.1677 (9)
C(F1)	−0.1773 (4)	0.1285 (8)	0.3966 (9)
C(F2)	−0.1810 (5)	0.2311 (8)	0.3390 (10)
C(F3)	−0.2397 (5)	0.2947 (9)	0.3416 (12)
C(F4)	−0.2910 (5)	0.2564 (9)	0.4073 (12)
C(F5)	−0.2867 (6)	0.1558 (10)	0.4727 (12)
C(F6)	−0.2297 (5)	0.0888 (8)	0.4642 (11)
C(F21)	0.3955 (4)	0.2159 (7)	0.4911 (9)
C(F22)	0.3781 (5)	0.1253 (8)	0.5634 (11)
C(F23)	0.4271 (6)	0.0586 (10)	0.6393 (12)
C(F24)	0.4960 (6)	0.0883 (10)	0.6433 (12)
C(F25)	0.5135 (5)	0.1765 (10)	0.5740 (12)
C(F26)	0.4646 (5)	0.2426 (8)	0.4966 (10)

zadodeca-1,4,8,11-tetraene)copper(II) dienolate. The geometry of the molecule with the numbering system is shown in Figure 1; atomic coordinates and bond lengths and angles are in Tables V and VI, respectively. Some least-squares planes and final thermal parameters for non-hydrogen atoms are in Tables VII and VIII (supplementary material).

The molecule in the crystal does not possess elements of internal symmetry, owing to the different conformation assumed by the two phenyl rings with respect to the C≡N groups. However, except for the torsion angles around C(5)–C(F21) and C(51)–C(F1), all geometrical parameters of the two parts of the molecule are identical within the experimental errors.

The coordination geometry of the Cu atom is square, the Cu, O, and N atoms being approximately on the same plane. The only angle that significantly deviates from the theoretical value is N(1)–Cu–N(11), 86.2 (3)°, as expected from the steric requirements of the CH_2CH_2 group. The two Cu–O distances are larger than those found in $[Cu\beta_2]$[3] and other similar compounds but are in good agreement along with the Cu–N distances with those in (*N*,*N'*-disalicylideneethylenediamine)copper.[21] The O(1)–C(1)–C(2)–C(3)–C(4)–C(5)–C(6)–N(2) moiety has a strict resemblance to the corresponding part of the $[Cu\beta_2]$[3] and $[Ni\beta_2]$[1] compounds. The whole molecule, with the exception of the two phenyl rings and the N(3) and N(31) atoms, is approximately planar. This, along with the bond distances, implies that some resonance extends from the Cu–O–C–C–C–N rings to the C═N groups. The two phenyl rings are planar within the experimental errors, and the bond distances and angles (mean 1.39 Å and 120.0°) are as expected.

Table VI. Bond Distances (Å) and Valence Angles (deg), with Esd's in Parentheses

Cu–O(1)	1.951 (8)	Cu–O(11)	1.931 (7)
Cu–N(1)	1.947 (7)	Cu–N(11)	1.963 (6)
O(1)–C(1)	1.33 (1)	O(11)–C(11)	1.31 (1)
C(1)–C(2)	1.40 (1)	C(11)–C(21)	1.42 (1)
C(2)–C(3)	1.43 (1)	C(21)–C(31)	1.43 (1)
C(3)–N(1)	1.30 (1)	C(31)–N(11)	1.31 (1)
N(1)–C(A2)	1.45 (1)	N(11)–C(A1)	1.48 (1)
C(A1)–C(A2)	1.50 (1)		
C(1)–C(6)	1.47 (1)	C(11)–C(61)	1.47 (1)
C(6)–N(2)	1.13 (1)	C(61)–N(21)	1.13 (1)
C(3)–C(4)	1.54 (1)	C(31)–C(41)	1.51 (1)
C(2)–C(5)	1.52 (1)	C(25)–C(51)	1.50 (1)
C(5)–N(3)	1.21 (1)	C(51)–N(31)	1.20 (1)
C(5)–C(F21)	1.48 (1)	C(51)–C(F1)	1.50 (1)
C(F21)–C(F22)	1.38 (1)	C(F1)–C(F2)	1.37 (1)
C(F22)–C(F23)	1.40 (1)	C(F2)–C(F3)	1.40 (1)
C(F23)–C(F24)	1.41 (1)	C(F3)–C(F4)	1.36 (1)
C(F24)–C(25)	1.34 (1)	C(F4)–C(F5)	1.38 (1)
C(F25)–C(26)	1.40 (1)	C(F5)–C(F6)	1.41 (1)
C(F26)–C(F21)	1.40 (1)	C(F6)–C(F1)	1.40 (1)

O(1)–Cu–O(11)	91.5 (3)	N(1)–Cu–N(11)	86.2 (3)
O(1)–Cu–N(1)	91.9 (3)	O(11)–Cu–N(11)	91.1 (3)
Cu–O(1)–C(1)	123.7 (7)	Cu–O(11)–C(11)	126.5 (7)
O(1)–C(1)–C(2)	128.4 (9)	O(11)–C(11)–C(21)	126.8 (8)
C(1)–C(2)–C(3)	123.0 (8)	C(11)–C(21)–C(31)	122.9 (7)
C(2)–C(3)–N(1)	121.8 (8)	C(21)–C(31)–N(11)	122.0 (7)
C(3)–N(1)–Cu	130.3 (6)	C(31)–N(11)–Cu	128.4 (6)
C(1)–C(6)–N(2)	178.2 (5)	C(11)–C(61)–N(21)	171.1 (9)
O(1)–C(1)–C(6)	115.3 (8)	O(11)–C(11)–C(61)	114.5 (8)
N(1)–C(3)–C(4)	120.6 (8)	N(11)–C(31)–C(41)	119.1 (8)
Cu–N(1)–C(A2)	109.6 (5)	Cu–N(11)–C(A1)	109.0 (5)
N(1)–C(A2)–C(A1)	109.4 (8)	N(11)–C(A1)–C(A2)	107.9 (7)
C(1)–C(2)–C(5)	117.8 (8)	C(11)–C(21)–C(51)	122.2 (7)
C(2)–C(5)–C(F21)	117.6 (8)	C(21)–C(51)–C(F1)	117.6 (8)
C(2)–C(5)–N(3)	120.9 (8)	C(21)–C(51)–N(31)	122.8 (8)
C(5)–C(F21)–C(F22)	123.9 (9)	C(51)–C(F1)–C(F2)	122.1 (9)

On the basis of spectral and magnetic data $[Cu(en(acac)_2(C_2N_2)_2)]$ is proposed to be isostructural with $[Cu(en(ba)_2(C_2N_2)_2]$.

The problem of the structure of $[Cu(papC_2N_2)Cl]$ and of the α and β forms of $[Ni(papC_2N_2)Cl]$ deserves a short comment.

The α species is formed by adding C_2N_2 to $[Ni(pap)Cl]$ either in water-saturated toluene (in this condition it is the only species that is formed) or in the early stages of the cyanation reaction in dry toluene.

The mixture of both species can be obtained rapidly in $C_2H_4Cl_2$. On the basis of the proposal that the primary reaction product should be α-$[Ni(papC_2N_2)Cl]$[1] and because of the strong similarity of the X-ray Debye spectra of β-$[Ni(papC_2N_2)Cl]$ and $[Cu(papC_2N_2)Cl]$, it appears reasonable to propose that the Cu^{II} compound is a β species. Attempts to isolate the α isomer of the Cu^{II} complex by shortening the reaction times failed.

General Comments. If follows from this study that the reaction of C_2N_2 with a nickel organometallic acetylacetonato ring discovered in 1979[1] is a rather general feature of the reactivity of this chemically rich small molecule with or-

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(21) Hall, D.; Waters, T. N. *J. Chem. Soc.* **1960**, 2644.

ganometallic rings containing active hydrogens at carbon atoms.

It appears from our studies on $[Cu(acac)_2]$[3] that the reaction requires a metal–oxygen ring opening, followed by C_2N_2 attack at the vacant site and its subsequent transfer to the coordinated ligand.

The reactivity trend found here, which is a function of the nature of the β-keto enolato ligand and of the metallic center, may well be in agreement with this metal-controlled mechanism.

The insertion reaction of electrophiles into the C–H methino bonds of the copper and nickel β-keto iminato rings was discovered in 1973.[22] Strong kinetic and/or thermodynamic effects on the overall process due to the nature of the metal and of the substituents in the rings have already been noticed.[9] For the tetradentate Schiff-base complexes Cu^{II} was found to be a more reactive metal center than Ni^{II}, in full agreement with our findings. A noticeable feature of the cyanogen reactivity is the strong tendency of the organometallic Schiff-base metal rings to undergo bis(cyanogen) addition without any preparative evidence of mono(cyanogen) addition products. This result contrasts with the findings relevant to (4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dionato)copper(II), for which the stepwise synthesis of mono- and diamino derivatives was possible[22] upon reaction with a variety of organic isocyanates.

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Registry No. $Cu(dbmC_2N_2)_2$, 82677-51-8; $Cu(en(acac)_2(C_2N_2)_2)$, 86365-10-8; $Cu(en(ba)_2(C_2N_2)_2)$, 86365-11-9; $Ni(en(ba)_2(C_2N_2)_2)$, 86365-12-0; Ni(pap)α, 82677-52-9; $Cu(eaa)_2$, 14284-06-1; $Cu(ba)_2$, 14128-84-8; $Cu(dbm)_2$, 14405-48-2; $Cu(en(acac)_2)$, 36885-37-7; $Cu(en(ba)_2)$, 15277-26-6; $Ni(en(acac)_2)$, 36802-27-4; $Ni(en(ba)_2)$, 53109-27-6; Cu(pap)Cl, 29966-36-7; Ni(pap)Cl, 29966-42-5; $Cu(acacC_2N_2)_2$, 77136-26-6; C_2N_2, 460-19-5; eaa, 141-97-9; ba, 93-91-4; dbm, 120-46-7; $en(acac)_2$, 6310-76-5; $en(ba)_2$, 16087-30-2; pap, 28484-27-7.

Supplementary Material Available: Listings of structure factor amplitudes, some least-squares planes, and final thermal parameters for non-hydrogen atoms (18 pages). Ordering information is given on any current masthead page.

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(22) Kenney, J. W.; Nelson, J. H.; Henry, R. A. *J. Chem. Soc., Chem. Commun.* **1973**, 690.

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Photoreactions of Rhodium(III) Complexes: The Cyanoammines $Rh(NH_3)_5CN^{2+}$ and *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$

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The photoreactions resulting from the ligand field excitation of the rhodium(III) cyanoammine complexes $Rh(NH_3)_5CN^{2+}$ and *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ are described. In each case, the reaction product in aqueous solution is the *cis*-$Rh(NH_3)_4(H_2O)CN^{2+}$ ion. The quantum yield for NH_3 aquation from $Rh(NH_3)_5CN^{2+}$ is 0.09 mol/einstein while the quantum yield for photoisomerization of *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ is 0.52 mol/einstein. These results are discussed in terms of theoretical models for ligand field excited-state reactions. Synthesis schemes and spectral properties for $Rh(NH_3)_5CN^{2+}$, *cis*- and *trans*-$Rh(NH_3)_4(CN)Cl^+$, and *cis*- and *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ are described as are the pK_a values for the latter ions. The rate constant for thermal Cl^- aquation from *trans*-$Rh(NH_3)_4(CN)Cl^+$ is also reported (3.6×10^{-4} s^{-1} at 25 °C, a value about 500-fold larger than that for $Rh(NH_3)_5Cl^{2+}$ under analogous conditions).

Introduction

The pentaamine and tetraamine complexes of rhodium(III), RhA_5Y^{n+} and *cis*- and *trans*-RhA_4XY^{m+} (A = NH_3 or an organic amine such as ethylenediamine/2), have proved especially valuable experimental models for the investigation of the ligand field (LF) photosubstitution reactions of d^6 hexacoordinate complexes (e.g., eq 1).[3] For such complexes both

$$\begin{aligned} RhA_5{}^{n+} + S &\xrightarrow{h\nu} RhA_5S^{3+} + Y^{(3-n)-} \\ &\xrightarrow{h\nu} RhA_4SY^{n+} + A \qquad (1) \end{aligned}$$

$$S = \text{solvent}$$

the emission spectroscopy and absorption spectroscopy can be characterized and give significant insight into the natures of the lower energy singlet and triplet excited states. Furthermore, in certain cases, not only the photosubstitution quantum yields but also the rates of the reactive deactivation processes from the ligand field excited states can be determined as functions of systemic parameters.[4,5] Such data serve as empirical tests of theoretical models for the photosubstitution reactions[6,7] and are now beginning to provide a more detailed mapping of the LF excited-state reaction mechanisms including both ligand labilization[8] and stereochemical rearrangement of the coordination sphere.[9] However, for nearly all the

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(3) (a) Ford, P. C. *Coord. Chem. Rev.* **1982**, *44*, 61–82. (b) Ford, P. C.; Wink, D.; DiBenedetto, J. *Prog. Inorg. Chem.* **1983**, *30*, 213–272.

(4) (a) Bergkamp, M. A.; Brannon, J.; Magde, D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4549–4554. (b) Bergkamp, M. A.; Watts, R. J.; Ford, P. C. *Ibid.* **1980**, *102*, 2627–2631.

(5) Sexton, D. A.; Skibsted, L. H.; Magde, D.; Ford, P. C. *J. Phys. Chem.* **1982**, *86*, 1758–1760.

(6) (a) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208. (b) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1978**, *17*, 2730.

(7) Hollebone, B. R.; Langford, C. H.; Serpone, N. *Coord. Chem. Rev.* **1981**, *39*, 181–224 and references therein.

(8) (a) Weber, W.; van Eldik, R.; Kelm, H.; DiBenedetto, J.; Ducommun, J.; Offen, H.; Ford, P. C. *Inorg. Chem.* **1983**, *22*, 623. (b) Skibsted, L. H.; van Eldik, R.; Kelm, H.; Weber, W.; Ford, P. C. *Ibid.* **1983**, *22*, 541.

(9) (a) Mønsted, L.; Skibsted, L. H. *Acta Chem. Scand.*, in press. (b) Howland, K.; Skibsted, L. H. *Ibid.*, in press.

0020-1669/83/1322-2749$01.50/0 © 1983 American Chemical Society