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Metal-Promoted Reactivity of Cyanogen toward Compounds Containing Active Hydrogens on Carbon. 1. Reaction of Cyanogen with Bis(2,4-pentanedionato)nickel(II)

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The reaction of cyanogen with bis(2,4-pentanedionato)nickel(II), [Ni(acac)$_2$], in CH_2Cl_2 at room temperature leads to a complex of formula [Ni(acac)$_2$(C_2N_2)$_2$] which, upon recrystallization, gives a square-planar monomeric complex containing the anion derived from the deprotonation of 2-(1-iminoethyl)acetoacetyl cyanide. Spectroscopic data and structural parameters derived from single-crystal X-ray analysis are reported. The reaction product before recrystallization is proposed to be bis(3-(cyanoiminomethyl)-2,4-pentanedionato)nickel(II), resulting from cyanogen insertion into the C–H methino bonds of the coordinated acac$^-$ ligands. Finally to support the idea of the rearrangement from bis(3-(cyanoiminomethyl)-2,4-pentanedionato)nickel(II) to bis[2-(1-iminoethyl)-1-cyano-1,3-butanedionato]nickel(II), we have obtained the first of these two species in alkaline medium from $NiCl_2$ and 3-(cyanoiminomethyl)-2,4-pentanedione. This ligand precursor has been characterized by us by IR, UV, and NMR techniques.

Introduction

The molecule of cyanogen is known to behave, in its coordination chemistry, as a Lewis base (nitrile-like) able to produce ligand displacement reactions, e.g., in nickel(0), rhodium(I), and ruthenium(II) complexes, and as an oxidative addition reagent toward electronically "dense" metallic centers.[2]

In the course of our studies on the problem of activation of cyanogen,[3-5] we have discovered a third kind of behavior of cyanogen in the coordination sphere of a metal, i.e., as an electrophile toward the organometallic rings produced by metal-coordinated 2,4-pentanedionato ligands, and very brief accounts on this subject have been published by us.[6] We have reported that C_2N_2 reacts with bis(2,4-pentanedionato)nickel(II), [Ni(acac)$_2$], to give a species of stoichiometry [Ni(acac)$_2$(C_2N_2)$_2$], which displays IR spectra clearly indicating that the cyanogen moiety, or part of it, has undergone insertion reaction onto the CH methino bonds to give C═N—H groups. The same reaction appears to occur with other bis- and tris(acetylacetonato)metal complexes of the first transition series and, remarkably, it does not occur with [Pd(acac)$_2$] and [Cr(acac)$_3$]. Finally, we reported that [Ni(acac)$_2$] is found to be a very efficient catalyst for the addition reaction of C_2N_2 to acetylacetone, Hacac, in CH_2Cl_2 to give a species of formula $C_7H_8N_2O_2$, certainly quite different in nature from the simple addition compound, 3-(cyanoiminomethyl)acetylacetone, which can be obtained by the EtO$^-$ catalyzed reaction of C_2N_2 with Hacac in ethanol at 0 °C.[7]

We wish to report here on the preparation and full characterization both of the primary reaction product between [Ni(acac)$_2$] and C_2N_2 in CH_2Cl_2 at ambient conditions and of an isomeric species resulting from the recrystallization procedure. Moreover, we wish to present our structural characterization of the β-diketone known for 80 years, 3-(cyanoiminomethyl)acetylacetone, but never employed as a ligand in its enolato form.

Experimental Section

Nominally anhydrous bis(2,4-pentanedionato)nickel was purchased from Merck Schuchardt and used as received. The solvents employed were reagent grade (Baker) and cyanogen was also a Baker reagent (98.5%, Union Carbide Linde Division).

Conveniently concentrated C_2N_2 solutions were prepared by sucking directly suitable amounts of the gas from the cylinder into the desired volume of dichloromethane. The C_2N_2 concentration was determined as previously described.[5]

Addition reactions to [Ni(acac)$_2$] were run in CH_2Cl_2, in closed vessels, containing the desired C_2N_2 concentration.

Infrared spectra were recorded on 257, 457, and 580 Perkin-Elmer instruments and electronic spectra were obtained by a Perkin-Elmer 572 and by a Cary 15. Melting points were determined by a Kofler apparatus and magnetic susceptibilities were determined at room temperature on a Gouy apparatus employing a Bruker B-M6 magnet coupled with a Sartorius electrobalance. The solid-state transparence spectra in the visible region were obtained as Nujol mulls or as KBr disks. Elemental analyses were performed in the microanalysis laboratories of our Institutes.

Preparation of "Crude" [Ni(acacC_2N_2)$_2$]. A 30-cm^3 sample of C_2N_2 solution in CH_2Cl_2 (~0.4 M) (~12 mmol) was added to 1.0 g of [Ni(acac)$_2$] (~4 mmol) under vigorous stirring at room temperature. The initially green solution turned gradually to brown and eventually to deep red in about 1 min. The stirring was, then, stopped and the solution was left to stand undisturbed for 1 h. We obtained a brick red microcrystalline precipitate, which was filtered off under vacuum with the exclusion of moisture, washed with CH_2Cl_2 (3 × 20 cm^3) and eventually dried under vacuum. The yield was 610 mg (~60%). The product is thermally stable up to 300 °C and is indefinitely stable in the laboratory atmosphere.

Anal. Calcd for $C_{14}H_{14}N_4NiO_4$: C, 46.50; H, 3.87; N, 15.50. Found: C, 46.39; H, 4.12; N, 15.29.

The experimental conditions can be modified, to some extent, with no effect on the nature of the product. Thus C_2N_2:[Ni(acac)$_2$] molar ratios can be changed from 2:1 to 6:1 and the reaction time shortened to 30 min.

Longer reaction times were not employed. The compound is scarcely soluble in the common organic solvents. It is fairly soluble in dimethyl sulfoxide.

The complex obtained was examined by visible–UV spectra in CH_2Cl_2, by IR spectra in KBr disks (or Nujol mulls), and by X-ray diffraction as powder.

Preparation of "Recrystallized" [Ni(acacC_2N_2)$_2$]. The "crude" complex (600 mg) was suspended in 150 cm^3 of $C_2H_4Cl_2$ (sym) at room temperature. The solvent was quickly brought to near its boiling temperature and then left under stirring until complete dissolution of the "crude" species had occurred. About 30 min after the beginning of the thermal treatment, the warm deep red solution was filtered rapidly on paper in warm glassware and left to cool very slowly at room temperature for a few hours. The dark red suspension obtained was, eventually, left at −18 °C overnight. A reddish yellow solution and a dark red crystalline precipitate were obtained. The latter was filtered off and carefully dried under vacuum (yield 400 mg). The product is thermally stable over 300 °C. The product appears as very brilliant dark red crystals, which can be stored indefinitely in the air.

Anal. Calcd for $C_{14}H_{14}N_4NiO_4$: C, 46.50; H, 3.87; N, 15.50. Found: C, 46.53; H, 4.05; N, 15.68.

The procedure always gave satisfactory elemental analysis for C, H, and N. A very pure sample of the complex, suitable for X-ray single-crystal diffraction analysis, was obtained by dissolving the "crude" species in the required volume of CH_2Cl_2 at room temperature. After filtration, the solution was left for about 45 days in a partially closed beaker at room temperature in the dark. The solubility is similar to that of the "crude" complex but somewhat smaller in CH_2Cl_2. The "recrystallized" complex was examined by visible–UV spectra in CH_2Cl_2, by visible spectra in Nujol mull, by IR spectra in KBr disks (or Nujol mulls), by X-rays as powder, and by the Gouy method as

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Table I. Crystal Data

$NiC_{14}H_{14}N_4O_4$
mol wt = 361.00
λ(Mo K$\bar{\alpha}$) = 0.7107 Å
a = 11.369 (7) Å
b = 11.555 (6) Å
c = 5.919 (4) Å
β = 99.1 (1)°
V = 767.69 Å^3
space group $P2_1/a$
D_c = 1.56 g cm^{-3}
Z = 2
μ(Mo K$\bar{\alpha}$) = 12.9 cm^{-1}

powder (three samples of different batches and controlled elemental analysis were examined).

Preparation of the Ligand $C_7H_8N_2O_2$ (3-(Cyanoiminomethyl)-acetylacetone). The method employed is from Traube[7a] and was more recently employed by Fackler.[7b]

Metallic sodium (50 mg) was added to absolute ethanol (40 cm^3) containing 5 cm^3 of acetylacetone, in a three-necked 100-cm^3 flask under nitrogen. After complete dissolution of the metal, the solution was kept at 0 °C for 20 min. After this time the atmosphere was evacuated for a few seconds by means of a mechanical pump. C_2N_2 was then admitted from the cylinder and the pressure in the reaction vessel was maintained at 1 atm for 20 min. Under vigorous stirring, an abundant white precipitate was obtained almost immediately, which gave rise to a very heavy yellow suspension, which was filtered off in the air under vacuum and washed with cold ethanol (3 × 20 cm^3). The supernatant solution was reddish yellow, but the precipitate appeared as a white powder rather soluble in benzene, dichloromethane, Me_2SO, and chloroform and less soluble in ethanol and ether. It is insoluble in *n*-hexane. The yield was 4.0 g (55%). The product melts at 128 °C (lit. 129–131 °C). It could be recrystallized by dissolution in hot ethanol, filtration, and slow crystallization at room temperature and then at −18 °C. One obtained white plates.

Anal. Calcd for $C_7H_8N_2O_2$: C, 55.26; H, 5.26; N, 18.42; O, 21.17. Found: C, 54.77; H, 5.39; N, 18.23; O, 22.06.

The crude compound can be normally obtained sufficiently pure. The compound tends to darken in the laboratory atmosphere and it has to be stored at −18 °C in the dark.

The compound was examined by visible–UV spectra in various solvents, by IR spectra in KBr disks (or Nujol mulls), and by NMR spectra in Me_2SO-d_6 and in $CDCl_3$.

Preparation of [Ni(acacC_2N_2)$_2$] from $NiCl_2{\cdot}6H_2O$ and 3-(Cyanoiminomethyl)acetylacetone in Alkaline Solution. To 300 mg of $C_7H_8N_2O_2$ ($\simeq$2 mmol) and 237 mg of $NiCl_2{\cdot}6H_2O$ ($\sim$1 mmol) was added 50 cm^3 of water. To the obtained suspension 2.5 cm^3 of a 1 M NaOH solution was added under vigorous stirring at room temperature. The green suspension of the ligand turned rapidly to a brick red and after 5 min the precipitate was filtered off under vacuum in the air, washed with water (3 × 20 cm^3), and dried under vacuum for some hours. The yield was 130 mg (38%). The product appears as a brick red powder. The elemental analysis was not satisfactory but clearly pointed to the composition $C_{14}H_{14}N_4NiO_4$.

Anal. Calcd: C, 46.50; H, 3.87; N, 15.50. Found: C, 43.76; H, 4.09; N, 13.54.

The crude product could be recrystallized from $C_2H_4Cl_2$ (symmetrical) as reported for the reaction product of [Ni(acac)$_2$] and C_2N_2, to give red crystals of satisfactory elemental analysis.

Anal. Calcd for $C_{14}H_{14}N_4NiO_4$: C, 46.50; H, 3.87; N, 15.50. Found: C, 46.44; H, 3.60; N, 15.40.

The compound was examined by vis–UV spectra in CH_2Cl_2 and by IR spectra in Nujol mull and KBr disks.

X-ray Structure Analysis and Refinement. Crystal data, obtained from single-crystal diffractometry, are listed in Table I.

The intensities were collected from a crystal of approximate dimensions 0.4 × 0.4 × 0.1 mm on a Philips PW1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 1.2°, scan speed = 0.02° s^{-1}). A total of 1342 independent reflections up to θ = 25° were measured, of which 1167 had intensities greater than 2.5 times their standard deviation (σ), σ being calculated from the counting statistics of the measurements.

During the data collection two standard reflections were measured every 180 min to check the stability of the crystal and electronics. Intensities were corrected for Lorentz and polarization effects and were then converted to an absolute scale by Wilson's method. An experimental absorption correction was applied following the method proposed by North, Phillips, and Mathews.[8]

The structure was determined by the heavy-atom technique. A Patterson synthesis revealed a Ni atom at the origin and four other peaks which were clearly Ni–O vectors. The positions of the remaining nonhydrogen atoms were derived from subsequent difference Fourier maps. The structure was refined by the full-matrix least-squares method, allowing the nonhydrogen atoms to vibrate anisotropically, and the R value was reduced to 0.06. A difference Fourier map yielded the positions of all H atoms, except for those bonded to the iminic nitrogen.

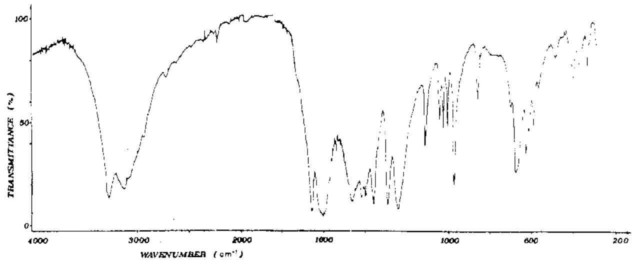


Figure 1. IR spectrum of 3-(cyanoiminomethyl)acetylacetone (αH) in KBr.

Table II. Remarkable IR Bands of 3-(Cyanoiminomethyl)acetylacetone

obsd band, cm^{-1}	intens	attribution[a]
3270	s	ν_{N-H} iminic
~3150	s, br	ν_{O-H} enolic
2235	vw	$\nu_{C\equiv N}$ nitrile
1655	s	$\nu_{C=N}$ $\alpha\beta$unsat
~1600	s	$\nu_{C=O}$ ketoenolic $\nu_{C=C}$ C=O conj

[a] Reference 12.

The refinement was carried out with the H atoms of the methyl groups constrained to their normal geometry by using the group refinement procedure.[9] The final R value for the 1167 observed reflections with $I > 2.5\sigma(I)$ was 0.047 (R_w = 0.057). Throughout the analysis the scattering factors of ref 10 were used; both the real and imaginary components of anomalous dispersion were included for nickel only.[10]

The refinement was carried out by minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, $w = 4.12[\sigma^2(F_o) + 0.001F_o^2]^{-1}$, to give average values of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) for groups of reflections independent of the value of $|F_o|$.

The calculations were carried out on the Cyber 76 computer of the "Centro di Calcolo Interuniversitario, Italia Nord-Orientale" with the SHELX76 system of crystallographic programs.[11]

Results and Discussion

The Nature of the EtO$^-$ Catalyzed Addition Reaction of C_2N_2 to Hacac. In 1898 Traube attributed to the reaction product between C_2N_2 and Hacac the nature of 3-(cyanoiminomethyl)acetylacetone (αH) resulting from the insertion reaction of C_2N_2 into one of the C–H bonds of carbon 3 in acetylacetone, reaction 1. The main evidence for this attribution was the ability of αH to give 3-(cyanomethyl)-acetylacetone upon reaction in water with the hydroxide ion, which acts as a scavenger of hydrogen cyanide. Fackler[7b] employed this base-promoted elimination reaction, to obtain 3-(cyanomethyl)acetylacetone, which was employed by this author to obtain a series of 3-cyanomethyl-substituted acetylacetonato complexes. In his paper the author expressed some doubts on Traube's attribution and he reported that he could not obtain any evidence for the presence of a C≡N group in the molecule on the basis of IR spectra.

$$(COCH_3)_2CH_2 + C_2N_2 \rightarrow (COCH_3)_2C(H)C(CN){=}NH \qquad (1)$$

We report here our spectral evidences, which support Traube's attribution on the chemical nature of αH.

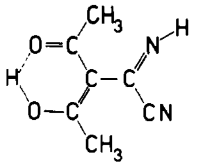
Infrared Spectrum. The IR spectrum is reported in Figure 1. The most indicative IR bands are summarized in Table II together with our tentative attributions.

Table III. Final Positional Parameters and Anisotropic Thermal Parameters (with Esd's in Parentheses) for Nonhydrogen Atoms[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0.5	0.5	0	33.2 (5)	20.5 (5)	33.2 (5)	−5.2 (3)	−8.5 (3)	2.9 (2)
O(1)	0.3863 (3)	0.5121 (2)	0.7411 (6)	49 (2)	37 (2)	48 (2)	−3 (1)	−8 (2)	0 (1)
O(2)	0.5501 (2)	0.3595 (2)	0.9145 (5)	41 (1)	28 (1)	42 (2)	−11 (1)	−11 (1)	7 (1)
N(1)	0.2465 (2)	0.2403 (3)	0.3510 (6)	28 (2)	29 (1)	48 (2)	−13 (1)	−11 (1)	−4 (1)
N(2)	0.1949 (4)	0.5075 (3)	0.2578 (9)	60 (3)	54 (3)	53 (3)	1 (2)	−16 (2)	8 (2)
C(1)	0.3578 (3)	0.4352 (3)	0.5857 (7)	34 (2)	29 (2)	28 (2)	1 (2)	1 (2)	−5 (1)
C(2)	0.4120 (3)	0.3239 (3)	0.5769 (7)	34 (2)	25 (2)	35 (2)	−4 (2)	0 (2)	−2 (1)
C(3)	0.5095 (3)	0.2937 (3)	0.7464 (7)	38 (2)	23 (2)	35 (2)	−5 (2)	4 (2)	1 (1)
C(4)	0.2652 (4)	0.4699 (3)	0.3980 (8)	38 (2)	30 (2)	41 (2)	−1 (2)	−6 (2)	0 (2)
C(5)	0.5737 (4)	0.1797 (4)	0.7541 (9)	53 (2)	33 (2)	54 (3)	−6 (2)	−1 (2)	16 (2)
C(6)	0.3540 (4)	0.2417 (3)	0.3996 (7)	55 (2)	26 (2)	33 (2)	−4 (2)	0 (2)	−4 (2)
C(7)	0.4270 (5)	0.1615 (5)	0.2734 (9)	64 (3)	54 (3)	51 (3)	−23 (2)	6 (2)	7 (2)

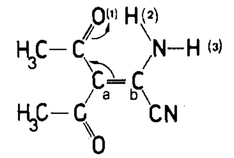
[a] The analytical temperature factor expression is $\exp[-2\pi^2(\Sigma_{ij}U_{ij}a_i^*a_j^*h_ih_j)]$.

The solid-state IR spectrum suggests the following structure for αH:



UV, NMR, and IR Spectra in Solution. The UV spectrum exhibits two bands at 245 nm (ϵ 4840) and 316 nm (ϵ 10070) in CH_2Cl_2, in which solvent the spectrum obeys Lambert–Beer's law in the range 1.3×10^{-5} to 1×10^{-3} M. The spectrum is in agreement with those reported for vinylogous amides.[13]

The NMR spectrum in Me_2SO-d_6 (at $\simeq$0.2 M) displays only two peaks at δ 2.33 and 9.45 (Me_4Si as internal standard). The first one can be attributed to methyl and the second one to amidic hydrogens. The integration ratio is 3:1. The data are in agreement with the structure



i.e., a vinylogous amide, in which the cyanoamido group is relatively free to rotate about the C_a–C_b partially double bond. Addition of small amounts of $CDCl_3$ to the Me_2SO solution causes the broadening of the peak at δ 2.33, which, for the 3:1 $CdCl_3$:Me_2SO volume ratio, produces two sharp peaks at δ 2.27 and 2.49, with identical area. The integration ratio among the two CH_3 groups and the amidic hydrogens results in 3:3:2. These data confirm the structure of αH as a vinylogous amide, "free" in Me_2SO and chelated in a $Me_2SO/CDCl_3$ mixture.

The IR spectrum of αH in $CDCl_3$ solutions slightly less concentrated than those employed for the NMR measurements ($\sim$0.08 M) confirms that αH is present largely as an amide, in which a significant hydrogen bond occurs between one of the two amidic hydrogens and the corresponding C=O group. A medium strong band at 3460 cm^{-1} can be attributed to the stretching N–H(3) and a medium strong, broad band centered at 3300 cm^{-1}, with slightly emerging peaks at 3370 and 3250 cm^{-1}, to the N–H(2) stretching, in which group H(2) interacts strongly with O(1).

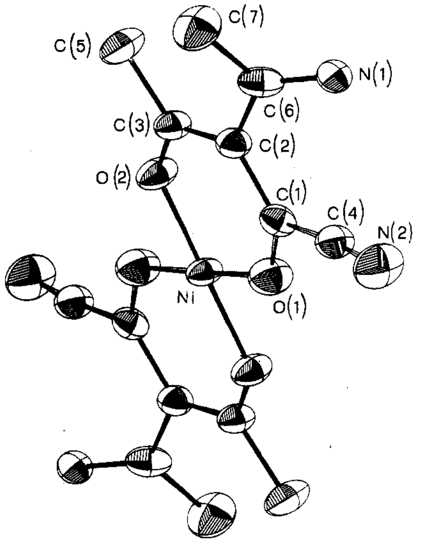


Figure 2. The molecular structure of $[Ni(acacC_2N_2)_2]$ ($Ni\beta_2$).

Table IV. Fractional Coordinates for the Hydrogen Atoms

	x	y	z
H'(C7)	0.5192 (5)	0.1879 (5)	0.3096 (9)
H''(C7)	0.3884 (5)	0.1912 (5)	0.1050 (9)
H'''(C7)	0.4217 (5)	0.0682 (5)	0.2800 (9)
H'(C5)	0.5016 (4)	0.1535 (4)	0.6226 (9)
H''(C5)	0.5833 (4)	0.1175 (4)	0.8920 (9)
H'''(C5)	0.6554 (4)	0.1839 (4)	0.6832 (9)
H(N1)			

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

Ni–O(1)	1.847 (3)	C(1)–C(4)	1.461 (5)
Ni–O(2)	1.818 (3)	C(3)–C(5)	1.503 (4)
O(1)–C(1)	1.283 (4)	C(2)–C(6)	1.490 (4)
O(2)–C(3)	1.279 (4)	C(6)–C(7)	1.517 (5)
C(1)–C(2)	1.431 (4)	C(4)–N(2)	1.142 (6)
C(2)–C(3)	1.416 (5)	C(6)–N(1)	1.211 (4)
O(1)–Ni–O(2)	92.6 (1)	C(1)–C(4)–N(2)	173.5 (4)
O(1)–Ni–O(2)	87.4 (1)	C(1)–C(2)–C(6)	117.0 (3)
Ni–O(1)–C(1)	127.4 (2)	C(3)–C(2)–C(6)	123.4 (3)
Ni–O(2)–C(3)	131.1 (2)	C(5)–C(3)–C(2)	124.0 (3)
O(1)–C(1)–C(2)	125.9 (3)	C(5)–C(3)–O(2)	112.6 (3)
C(1)–C(2)–C(3)	119.3 (3)	C(2)–C(6)–C(7)	121.4 (3)
C(2)–C(3)–O(2)	123.3 (3)	C(2)–C(6)–N(1)	119.5 (3)
O(1)–C(1)–C(4)	115.2 (3)	C(7)–C(6)–N(1)	119.1 (3)
C(2)–C(1)–C(4)	118.8 (3)		

Reaction Product between C_2N_2 and $[Ni(acac)_2]$. The Recrystallized Species. Reaction of $[Ni(acac)_2]$ with 2 molar equiv of cyanogen in dichloromethane yields a brick red complex of formula $[Ni(acacC_2N_2)_2]$. A compound with the same solid-state IR spectrum and with extremely similar UV–vis spectra in CH_2Cl_2 can be obtained from $NiCl_2$ and α^- in water (see the Experimental Section). Both samples give upon recrystallization from hot $C_2H_4Cl_2$ the same species, i.e., a dark red crystalline product being analyzed exactly as $[Ni(acacC_2N_2)_2]$ but displaying solid-state IR spectra noticeably different from those of the "crude" species obtained through the two completely different synthetic procedures. The X-ray powder spectra (Debye) of the "crude" and

Table VI. Some Least-Squares Planes[a] in the Complex with Their Dihedral Angles (deg) and Deviations (Å) of the Atoms to the Respective Planes

Plane A:	$0.6167X + 0.7434Y + 0.2589Z = 7.8007$		
Ni	0	C(1)*	−1.006
O(1)	0	C(2)*	−1.590
O(2)	0	C(3)*	−1.007
O(1)′	0		
O(2)′	0		
Plane B:	$0.7375X + 0.3963Y - 0.5469Z = 2.7066$		
O(1)	−0.003	C(2)	−0.012
O(2)	−0.003	C(3)	0.009
C(1)	0.009		
Plane C:	$0.1494X + 0.6981Y - 0.7002Z = 0.8684$		
N(1)	0.003	C(6)	−0.009
C(2)	0.003	C(7)	0.003

Dihedral Angles (deg)

plane A–plane B	52.6	plane A–plane C	64.5
plane B–plane C	39.7		

[a] The equations of the planes are in the form $AX + BY + CZ = D$, in orthogonal Å space with X parallel to a, Z perpendicular to a in the ac plane, and Y perpendicular to the ac plane. An asterisk denotes an atom not used in the plane calculation.

Table VII. Shorter Intramolecular Nonbonded Distances (Å)

O(1)...O(2)	2.65	N(1)...C(4)	2.67
O(1)...O(2′)	2.53	N(1)...N(2)	3.17
C(5)...C(7)	3.07		

"recrystallized" species (both obtained from C_2N_2) are also very different, both indicating a crystalline nature of both materials. The visible–UV spectra of the "crude" and "recrystallized" species in CH_2Cl_2 and in the solid state are practically identical.

X-ray Structure. A single-crystal X-ray analysis of the "recrystallized" species was carried out.

The molecular structure of $Ni\beta_2$ as it occurs in the crystal is shown in Figure 2. The final structural parameters with their esd's of nonhydrogen and H atoms are reported in Tables III and IV, respectively. The bond lengths and valence angles are given in Table V. Some least-squares planes and the shorter intramolecular nonbonded distances are listed in Tables VI and VII, respectively. The coordination geometry of the nickel atom is square, the nickel and the four oxygen atoms being strictly on the same plane as required by crystallographic symmetry. Therefore the only departure from the exact square-planar configuration is represented by the different values of the two O–Ni–O angles 87.4 (1) and 92.6 (1)°, respectively. This disagreement can be easily justified by the geometric requirements of the acetylacetonato ligand. Moreover, the OCCCO portion of the structure is also planar and this plane is bent at an angle of 127.4° with respect to the OMO plane.

The two Ni–O distances are significantly different, as a consequence of the inductive effect due to the C≡N group, which apparently has a weakening effect on the Ni–O(1) bond.

The mean of the two Ni–O distances, 1.833 Å, shows a significant shortening, as compared to Ni–O bond lengths in other Ni^{II} complexes, particularly in the closely related $[Ni(acac)_2]_3$[14a] and $[Ni(acac)_2(H_2O)_2]$[14b] (2.01 and 2.015 Å, respectively) but it is equal, within the experimental error, to the mean Ni–O bond length (1.836 (5) Å) in bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II),[15] i.e., bis(dipivaloylmethanato)nickel(II).

This result is in line with the already reported observation,[15] according to which the Ni–O distances are shorter by approximately 0.1 Å in a square-planar nickel(II) complex than in corresponding octahedral ones.

The acetylacetonato moiety has dimensions very similar to those in other $C_5H_7O_2M$ moieties.[15-17]

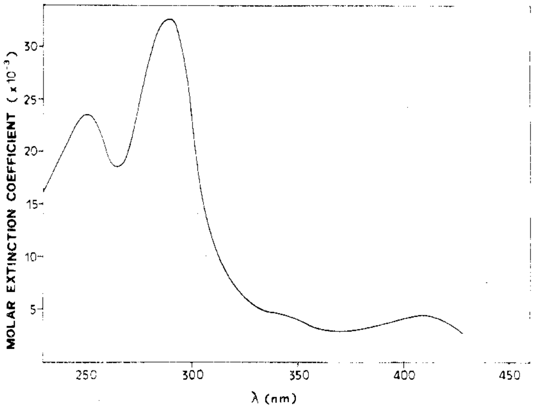


Figure 3. UV spectrum of $Ni(acacC_2N_2)_2$ ("recrystallized") in CH_2Cl_2 at room temperature.

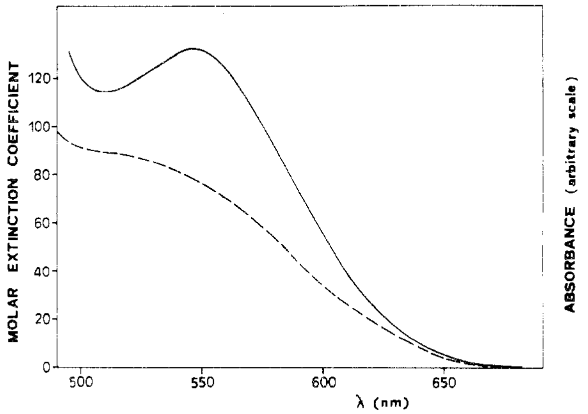


Figure 4. Visible spectrum of $Ni(acacC_2N_2)_2$ "recrystallized" in CH_2Cl_2 (—) and in solid (---) at room temperature.

Table VIII. Visible–UV Spectral Data for $Ni\beta_2$[a]

λ, nm	ε, M^{-1} cm^{-1}	λ, nm	ε, M^{-1} cm^{-1}
253	19.400	415	4.500
290	30.250	555	129
340	4.500		

[a] Average figures of several independent measurements.

As regards the substituents, the $C(3)(sp^2)$–$C(5)(sp^3)$ bond value, 1.503 (4) Å, is very close to that of the standard single bond.[18] The dimensions of the cyano group are in the range that has been reported for this kind of compound.[18]

The C(6)=N(1) bond length, 1.211 (4) Å, is shorter than the value derived from covalent radii sum.[18] This, along with the value of C(2)–C(6), which is very close to a standard $C(sp^2)$–$C(sp^2)$ single bond value and with the value of the dihedral angle about C(2)–C(6), 39.7°, indicates that no resonance extends from the imino group to the acac moiety.

The crystal packing is determined by van der Waals forces and none of the contacts are shorter than the sum of the relevant van der Waals radii.

Spectroscopic Properties. The visible–UV spectra in CH_2Cl_2 are reported in Figures 3 and 4.

The spectrophotometric features of $Ni\beta_2$ are summarized in Table VIII. Solutions from 2×10^{-5} to 5×10^{-4} M obey Lambert–Beer's law in the visible–UV range. No evidence of any absorption band different from the "red" one could be obtained for 5×10^{-4} M solutions as far as 1300 nm (10-cm cells).

The band at 555 nm (observed also in the solid state) corresponds closely to that at 526 nm observed for the dipivaloylmethanato complex and to that at 555 nm observed for monomeric $[Ni(acac)_2]$ above 150 °C in diphenylmethane.[19c] The data obtained in solution in the visible region

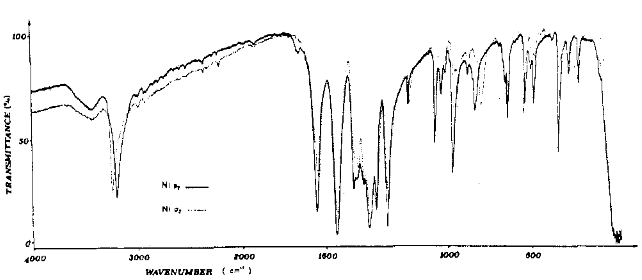


Figure 5. IR spectrum of $Ni\alpha_2$ (···) and $Ni\beta_2$ (—) in KBr.

appear, on the other hand, sufficiently unambiguous to exclude the presence of significant concentrations of a trimeric octahedral species in equilibrium with the monomeric one.

The IR spectrum in KBr disks is reported in Figure 5 just on that of the "crude" complex.

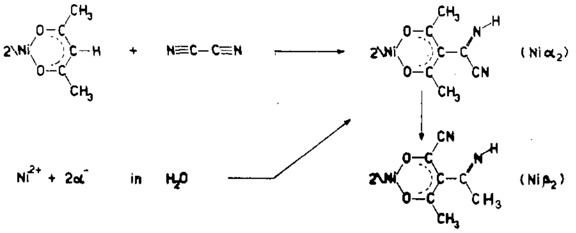
The IR bands, the most important of which are reported in Table IX, are in agreement with the determined structure. The unattributed bands at 1065, 1035, 975, 875, and 720 cm^{-1} are reported only for the sake of comparison with the spectrum of the "crude" species.

Two IR features appear to be remarkable, i.e., the 3200-cm^{-1} iminic band, which falls rather closely to that of solid αH (3270 cm^{-1}) thus supporting indirectly the attribution of the 3270-cm^{-1} band for αH, and the almost undetectable $\nu_{C\equiv N}$ band at 2235 cm^{-1}, which confirms the quenching effect due to the presence of an oxygen atom in the proximity of a C≡N group reported in the literature.[12] Finally, a rather surprising result appears to be the observed magnetic behavior exhibited by the complex. The effective magnetic moment measured for the complex is, in fact, 0.54 μ_B (the average values of three independent measurements on three different samples are 0.42, 0.70, and 0.51 μ_B, respectively). On consideration of the perfect planarity of the group OONiOO, this figure has to be due to a TIP contribution.

The Primary Reaction Product between $[Ni(acac)_2]$ and C_2N_2. The "Crude" Species. The structure of the "recrystallized" species reported in Figure 2 is certainly very surprising, in that the reasonable analogy with the reactions recently described by Nelson et al.[20] between $[Ni(acac)_2]$ and various electrophiles to give 3-substituted trimeric acetylacetonato complexes (eq 2) made reasonable the expectation

(2)

of obtaining a 3-(cyanoiminomethyl)acetylacetonato complex and not a derivative of the 1-(2-iminoethyl)acetoacetyl cyanide anions (eq 3). We think that the primary reaction product



(3)

is, in fact, the expected species, which then evolves either rapidly in hot $C_2H_4Cl_2$ or slowly in CH_2Cl_2 at room temperature to the more stable $Ni\beta_2$ species (eq 3).

The solid-state IR spectrum of the "crude" product is reported in Figure 5 and the most significant IR bands are reported in Table X.

The comparison of the data of Table IX with those of Table X and inspection of Figure 5 show that the "crude" and "recrystallized" species are certainly different to a significant extent in the solid state. (It seems worthwhile to underline the 3245-cm^{-1} value for ν_{N-H} (3270 cm^{-1} for αH and 3200 cm^{-1} for $Ni\beta_2$) and the clearly enhanced intensity of the C≡N stretching band, as expected on considering that the C≡N groups in $Ni\alpha_2$ are farther from the oxygen atoms than in $Ni\beta_2$.) This finding, coupled with the difference observed in the Debye spectra, indicates that $Ni\alpha_2$ and $Ni\beta_2$ are either *molecular isomeric species* or solid-state *dimorphic compounds*.

Table IX. Remarkable IR Bands of the "Recrystallized" Complex

obsd band, cm^{-1}	intens	attribution[b]
3200	s	ν_{N-H} iminic
2235	vw	$\nu_{C\equiv N}$ nitrile
1640	s	$\nu_{C=N}$ iminic
1545	s	$\nu_{C=O}$ ketoenolic
1065	m[a]	
1035	w[a]	
975	m	
875	m	
720	m	

[a] Doublet of different intensity. [b] Reference 12.

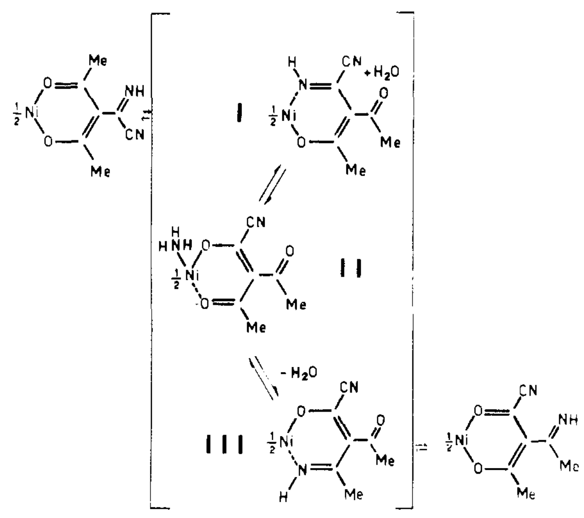
Table X. Remarkable IR Bands of the "Crude" $[Ni(acacC_2N_2)_2]$ Complex

obsd bands, cm^{-1}	intens	attribution[b]
3245	s	ν_{N-H} iminic
2220	vw	$\nu_{C\equiv N}$ nitrile
1635	s	$\nu_{C=N}$ iminic
1545	s	$\nu_{C=O}$ ketoenolic
1065	m[a]	
1035	m[a]	
970	m	
845	m	
725	m	

[a] Doublet of equal untensity. [b] Reference 12.

The vis-UV spectra of $Ni\alpha_2$ and $Ni\beta_2$ in CH_2Cl_2 and in the solid state are practically identical (λ_{max} at 555 nm in CH_2Cl_2 with ϵ 130 M^{-1} cm^{-1} for [Ni] = 10^{-3} M) and, therefore, these features do not help in the choice between the two hypotheses. It is well-known, in fact, that the UV spectra of acetylacetonato complexes ($\pi \rightarrow \pi^*$ and charge-transfer transitions) are not very dependent on the substitution on the ring,[19] as it is particularly exemplified by the cases of the Cr^{III} and Fe^{III} tris complexes containing either acetylacetonato or 1,1,1-trifluoroacetylacetonato ligands,[21,22] in which complexes the λ_{max} shifts in UV are about 10 nm. Moreover, the coincidence of the single broad bands around 550 nm observed for $Ni\alpha_2$ and $Ni\beta_2$ can be expected on considering that the corresponding band in $[Ni(acac)_2]$ (monomeric species present in diphenylmethane above 150 °C) and in bis(dipivaloylmethanato)nickel(II) differ by 30 nm.[19c]

The remarkable finding that, in our opinion, supports the proposal for the isomerism is the fact that $Ni\alpha_2$ can be obtained both from $[Ni(acac)_2]$ and C_2N_2 (thanks to its scarce solubility and to the mild conditions employed for the preparative reaction) and *directly* from αH and Ni^{2+} in alkaline aqueous medium. It would appear, in fact, very unlikely that the *same* species ($Ni\alpha_2$) in the *same* dimorphic crystalline structure could be obtained through two completely different synthetic procedures (differing in particular for the solvent employed!). To conclude, it seems worthwhile to try to put forward a tentative hypothesis for the mechanism of ligand rearrangement in the conversion $Ni\alpha_2 \rightarrow Ni\beta_2$. We think that traces of water present in the solvent employed for the recrystallization procedure could cause hydrolysis of the imino groups present in $Ni\alpha_2$. A tentative reaction pathway for a water-catalyzed $Ni\alpha_2 \rightarrow Ni\beta_2$ interconversion is reported in eq 4. $Ni\alpha_2$ isomerizes preliminarly to I, which undergoes water



(4)

attack, >C=NH hydrolysis, and ammonia extraction to give a diaminobis(triketoenolate) complex, II. This species can undergo ammonolysis of the metal-coordinated CO groups to give either I or III, which isomerizes to the more stable species $Ni\beta_2$.

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Registry No. $Ni\alpha_2$, 71616-26-7; $Bi\beta_2$, 71616-27-8; αH, 71616-10-9; $Ni(acac)_2$, 3264-82-2; C_2N_2, 460-19-5; acac, 123-54-6.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Istituto di Chimica Analitica. (b) Istituto di Chimica Organica.

(2) For a review on the subject see B. Corain, M. Basato, and A. Warsame, *Chim. Ind.* (*Milan*), **61**, 567 (1979).

(3) M. Bressan, G. Favero, B. Corain, and A. Turco, *Inorg. Nucl. Chem. Lett.*, **7**, 203 (1971).

(4) G. Favero, B. Corain, P. Rigo, and A. Turco, *Gazz. Chim. Ital.*, **103**, 297 (1973).

(5) B. Corain, M. Basato, and G. Favero, *J. Chem. Soc., Dalton Trans.*, 2081 (1977).

(6) (a) B. Corain, *J. Organomet. Chem.*, C19 (1978). (b) B. Corain, Proceedings of the 11th National Congress of Inorganic Chemistry, Arcavacata di Rende, Italy, 1978.

(7) (a) W. Traube, *Chem. Ber.*, **31-3**, 2938 (1898); (b) J. P. Fackler, Jr., *J. Chem. Soc. A*, 1957 (1962).

(8) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24**, 351 (1968).

(9) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(10) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

(11) G. Sheldrick, "SHELX 76" System of Computing Programs, University of Cambridge, England, 1976.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 3rd ed., Chapman and Hall, London, 1975.

(13) F. Filira, M. Acampora, V. Giormani, M. Rothstein, and F. D'Angeli, *Gazz. Chim. Ital.*, **107**, 479 (1977).

(14) (a) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961); (b) H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 1481 (1964).

(15) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966), and references therein.

(16) B. L. Barnett and C. Krüger, *J. Organomet. Chem.*, **42**, 169 (1972).

(17) F. A. Cotton, B. A. Frenz, and D. L. Hunter, *J. Am. Chem. Soc.*, **96**, 4820 (1974).

(18) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

(19) For the chemical, structural, and spectroscopic properties of (acetylacetonato)metal complexes see (a) J. P. Collman, *Angew. Chem., Int. Ed. Engl.*, **4**, 132 (1965); (b) J. P. Fackler, Jr., *Prog. Inorg. Chem.*, **7**, 361 (1966); (c) D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969); (d) K. C. Joshi and V. N. Pathak, *ibid.*, **22**, 37 (1978).

(20) R. P. Eckberg, J. H. Nelson, J. W. Kenney, P. N. Howells, and R. A. Henry, *Inorg. Chem.*, **16**, 3128 (1977).

(21) A. M. Fatta and R. L. Lintvedt, *Inorg. Chem.*, **10**, 478 (1971).

(22) R. L. Lintvedt and L. K. Kernitsky, *Inorg. Chem.*, **9**, 491 (1970).

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Unusual Sulfur Insertion in a Copper(I)–Mercaptobenzothiazole Complex: Synthesis and Structural Study of $[Cu^I(C_7H_5NS_2)(C_{14}H_8N_2S_5)](ClO_4)\cdot 2CHCl_3$

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The title complex was obtained from a chloroform solution of mercaptobenzothiazole (Hmbt) which was reacted with solid copper(II) perchlorate hexahydrate. The infrared spectrum of this species was consistent with the presence of the ligand under two different forms such as Hmbt and mbt, involving different coordination sites. This was confirmed by an X-ray structure determination which also revealed an unusual sulfur insertion. Crystals are monoclinic, of space group $P2_1/C$, with $a = 14.746$ (6) Å, $b = 10.883$ (5) Å, $c = 12.296$ (6) Å, and $\beta = 94.51$ (1)°. The structure was solved by the heavy-atom method. The final agreement index R_w was 0.06. The perchlorate anion exhibits a statistical distribution between two sites, in the ratio 0.65/0.35. The cuprous complex cation is tetrahedral; it contains mercaptobenzothiazole under two different forms: (i) a Hmbt form S bonded to the metal through the exocyclic sulfur atom (Cu–S = 2.221 (4) Å) and (ii) an unusual oxidized form RSSSR in which an additional sulfur atom has been inserted. This mbt–S–mbt unit is coordinated through both thiazolic nitrogen atoms (Cu–N = 2.04 (1), 2.01 (1) Å) and the central sulfur atom (Cu–S = 2.486 (4) Å). The molecular structure of both forms is discussed.

Introduction

During the last few years, we have been interested in the interaction of organic corrosion inhibitors such as mercaptobenzothiazole (Hmbt) with metallic copper surfaces. For elucidation of the stereochemical aspect of this interaction, models of the surface complex were first derived from carbonyl clusters,[1] with $Ru_3(CO)_{12}$ as a starting material. The most interesting coordination type was found in the triangular cluster $Ru_3H(CO)_9(mbt)$. The infrared spectrum of this complex was closely related to the reflection spectrum of the actual surface complex. Although such a species may be considered as a good model of the ligand's linkage on a bulk metal surface, it concerns ruthenium and not copper.

A second move in our investigation was then to prepare copper complexes in order to check the affinity of the ligand for this metal. Let us first note that recent developments in copper–thiol cluster chemistry[2-4] provide several new compounds which seem interesting for this purpose. The formation

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