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Nitromalonaldehyde as a Ligand. Synthesis and Reactivity with Isocyanides of Monomeric Tris(ligand)metal(II) Complexes and Crystal Structure of Pentakis(4-methylphenyl isocyanide)cobalt(I) Tris(nitromalonaldehydo)cobaltate(II)

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The syntheses and characterization of the first monomeric tris(β-dicarbonyl) species of cobalt(II) and iron(II) have been achieved by using nitromalonaldehyde (NMA) as the ligand. The reaction between NMA and several other metal(II) chlorides (M = Zn, Ni, Cu, Pt, Pd) is also presented, and the results are tentatively explained on the basis of both steric and electronic properties of the dialdehyde ligand compared with various substituted acetylacetonates. Furthermore, the reactivity of some nitromalonaldehyde complexes with isocyanides has been investigated, and a new method to synthesize the $[Fe(CNR)_6]^{2+}$ and $[Cu(CNR)_4]^+$ cations is described. In the case of (nitromalonaldehyde)cobalt(II) complexes, reaction with isocyanides gives $[Co(CNR)_5][Co(NMA)_3]$ (R = 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-$NO_2C_6H_4$, 4-ClC_6H_4). The crystal structure of $[Co(4\text{-}CH_3C_6H_4NC)_5][Co(NMA)_3]$ is built up of discrete monomeric octahedral $[Co(NMA)_3]^-$ anions and trigonal-bipyramidal $[Co(CNR)_5]^+$ cations. The crystals are triclinic, of space group $P\bar{1}$, with unit cell dimensions a = 14.29 (1) Å, b = 16.60 (1) Å, c = 12.19 (1) Å, α = 109.2 (1)°, β = 110.0 (1)°, γ = 94.1 (1)°, and Z = 2. A total of 1942 observed reflections have been measured by single-crystal diffractometry and refined by full-matrix least squares to R = 0.109.

Introduction

A large number of studies on synthesis, structure, molecular association, and reactivity of β-dicarbonyl complexes have been reported.[1] However, few data are known on the chelating properties of dialdehydes which can be considered the simplest 1,3-dicarbonyl ligand. Except for the work of Collman[2] on tris(malonaldehyde)chromium(III) and of Osman[3] on the stability of nickel(II) and copper(II) malonaldehyde complexes, no other metal chelates with this ligand or with its γ-substituted derivatives has been reported. It seemed therefore desirable to examine the ligand properties of nitromalonaldehyde (NMA) by synthesizing new complexes and to better understand the influence of steric and electronic factors on the properties of such compounds by comparison with the complexes of β-diketones.

The behavior of bis(β-diketonate)metal(II) complexes as Lewis acids to form five- or six-coordinate adducts with neutral donor molecules, as well as the reactions characteristic of aromatic systems on the chelate rings, is known.[4] However, although the interaction in solution between π-bonding ligands such as phosphines and isocyanides and paramagnetic cobalt(II) and nickel(II) acetylacetonate complexes have been studied by ^1H NMR technique,[5] very little attention has been paid to the isolated reaction products of β-dicarbonyl complexes with π-bonding ligands. We have previously reported[6] on the chemistry of iron(II) and cobalt(I) isocyanide compounds, and, as an extension of these studies, we have investigated the reactivity of some nitromalonaldehyde complexes with isocyanides in an attempt to obtain stable adducts and/or the products formed by substitution of the chelate ligand.

Thus we synthesized $[Co(CNR)_5][Co(NMA)_3]$ (R = $CH_3C_6H_4$) whose X-ray crystal structure has been compared with those of the tetramer $[Co(acac)_3]_4$ (acac = acetylacetonate)[7] and its adduct $[Co(acac)_2(H_2O)_2]$.[8]

Experimental Section

Material and Apparatus. Sodium nitromalonaldehyde monohydrate [Na(NMA)·H_2O] was prepared from mucobromic acid following the procedure reported.[9] Substituted phenyl isocyanides were obtained by the phosgene method of Ugi et al.[10] All the solvents used were dried and purified by standard methods. The other chemicals were used as received.

Infrared spectra of KBr pellets and dichloromethane solutions were recorded on Perkin-Elmer 621 or 457 spectrophotometers. Proton NMR spectra were obtained with use of a Varian EM 390 instrument with tetramethylsilane as internal standard. Electronic spectra at room temperature were recorded with use of a Perkin-Elmer Coleman 575 spectrophotometer. Magnetic susceptibility were measured on solid samples by Gouy standard techniques and in solution by the Evans method.[11] Conductivities of 10^{-3} M solutions of complexes were measured with an LKB conductivity bridge at 25 °C.

Preparation of Complexes. $[M(NMA)_2 \cdot nH_2O]$ (M = Zn(II), Ni(II), Co(II), Fe(II); n = 2–4) and $Cu(NMA)_2$. To an aqueous solution (10 mL) of the metal(II) chloride (10 mmol) was added dropwise at room temperature a solution of 3.14 g (20 mmol) of Na ($C_3H_2NO_4$)·H_2O in 20 mL of water. Although a precipitate formed immediately, the reaction mixture was stirred for 1 h and then cooled at 5 °C. After filtration, the product was recrystallized by acetone–diethylether (yield ca. 60%). With copper chloride after crystallization, the insoluble $[Cu(NMA)_2]$ complex was obtained. Anal. Calcd for $[Zn(NMA)_2(H_2O)_3]$: C, 20.50; H, 2.87; N, 7.97. Found: C, 20.06; H, 2.53; N, 7.59; mp 235 °C. Calcd for $[Ni(NMA)_2(H_2O)_4]$: C, 19.86; H, 3.33; N, 7.72. Found: C, 19.71; H, 3.46; N, 7.84; mp >270 °C. Calcd for $[Co(NMA)_2(H_2O_3)]$: C, 20.88; H, 2.92; N, >270 Found: C, 20.60; H, 2.58; N, 7.99; mp >270 °C. Calcd for $[Fe(NMA)_2(H_2O)_2]$: C, 22.24; H, 2.49; N, 8.65. Found: C, 22.22; H, 2.46; N, 8.73; mp 225 °C.

$[M(NMA)_2]$ (M = Zn(II), Ni(II), Co(II), Fe(II)). The bis(nitromalonaldehyde) complexes were easily obtained from the corresponding water adducts by heating at 110 °C under vacuum for 2 h.

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$[M(NMA)_2(py)_2]$ (M = Co(II), Ni(II), Zn(Ii)). A large excess of pyridine was added at room temperature to a solution of $[M(NMA)_2 \cdot nH_2O]$ (2 mmol) in 10 mL of acetone. By adding diethyl ether, the products precipitated immediately, and they were crystallized by anhydrous ethanol under nitrogen [Co(II), Ni(II) derivatives] or by acetone–diethyl ether [Zn(II) derivative] (yield ca. 70%). Anal. Calcd for $[Zn(NMA)_2(py)_2]$: C, 42.17; H, 3.10; N, 12.29. Found: C, 41.97; H, 2.80; N, 11.97; mp 213 °C dec. Calcd for $[Ni(NMA)_2(py)_2]$: C, 42.79; H, 3.14; N, 12.48. Found: C, 42.80; H, 3.26; N, 12.31; mp 190 °C. Calcd for $[Co(NMA)_2(py)_2]$: C, 42.77; H, 3.14; N, 12.47. Found: C, 42.20; H, 3.29; N, 12.37; mp 192 °C.

$AsPh_4[M(NMA)_3]$ (M = Co(II), Fe(II)). An aqueous solution (50 mL) containing 4.6 g (30 mmol) of $[Na(NMA) \cdot H_2O]$ was added at room temperature to $[MCl_2 \cdot nH_2O]$ (10 mmol) in 90 mL of water. The $[M(NMA)_2 \cdot nH_2O]$ complex immediately precipitated and was removed by suction filtration. The addition of $[AsPh_4]Cl$ to the reaction mixture caused the precipitation of a red product which was recrystallized by acetone–diethyl ether (yield ca. 40%).

$Y[PtCl_2(NMA)]$ (Y = K, $AsPh_4$). A solution of 0.83 g (2 mmol) of K_2PtCl_4 and 0.24 g (1.5 mmol) of $[Na(NMA) \cdot H_2O]$ in 10 mL of water was stirred for 3 h at 40 °C. By cooling the reaction mixture at 5 °C, pale yellow crystals of $K[PtCl_2(NMA)]$ were obtained which were recrystallized from water (yield ca. 50%). The corresponding $AsPh_4[PtCl_2(NMA)]$ complex was prepared by adding $[AsPh_4]Cl$ to a solution of the potassium salt in water.

$[Pd(NMA)_2]$. This compound was prepared at room temperature following the method reported for the platinum(II) complex. Its low solubility in water and in organic solvents prevented recrystallization.

$[Co(CNR)_5][Co(NMA)_3]$ (R = 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-$NO_2C_6H_4$, 4-ClC_6H_4). The isocyanide (8 mmol) was added at room temperature to a solution of 0.69 g (2 mmol) of $[Co(NMA)_2 \cdot 3H_2O]$ in 30 mL of acetone. The reaction mixture was vigorously stirred for 40–80 min until the color of the solution changed from pink to orange-red. The dropwise addition of 200 mL of diethyl ether caused the precipitation of a crude product which was crystallized by ethanol (yield ca. 40%). The 4-$NO_2C_6H_4NC$ compound was purified by acetone–diethyl ether.

Special care must be taken to crystallize these derivatives. The temperature must be kept below 50 °C in order to avoid any decomposition.

$[Co(CNR)_5][Co(hfac)_3]$ (R = 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$; hfac = Hexafluoroacetylacetonate). These compounds have been prepared with the same method reported above for the analogous NMA derivatives.

The starting complex $[Co(hfac)_2 \cdot 2H_2O]$ was obtained by treatment of (10 mmol, 2.38 g) of $CoCl_2 \cdot 6H_2O$ and hexafluoroacetylacetone (20 mmol) in 50 mL of water with 20 mmol of NaOH. The precipitated product was used without further purification.

$[Cu(4\text{-}CH_3C_6H_4NC)_4]ClO_4$ and $[Fe(4\text{-}CH_3C_6H_4NC)_6](ClO_4)_2$. To an ethanol suspension (80 mL) of 10 mmol of $[Cu(NMA)_2]$ or of $[Fe(NMA)_2(H_2O)_2]$ was added 7.1 g (60 mmole) of 4-tolyl isocyanide. After the reaction mixture was stirred for 1 h, anhydrous lithium perchlorate was added, and the solution was concentrated to about 20 mL. The crude product which separated out was recrystallized from anhydrous ethanol (yield ca. 70%).

Collection and Reduction of X-ray Data. Preliminary unit cell dimensions and space group information were determined from rotation and Weissenberg photographs. Accurate unit cell parameters, with estimated standard deviations, were obtained by a least-squares refinement of 2θ values for 17 reflections measured on a single-crystal Siemens AED diffractometer. Crystallographic data are as follows: $C_{49}H_{50}Co_2N_8O_{12}$, triclinic, $M_r = 1060.85$; $a = 14.29$ (1), $b = 16.60$ (1), $c = 12.19$ (1) Å; $\alpha = 109.2$ (1), $\beta = 110.0$ (1), $\gamma = 94.1$ (1)°; $V = 2510$ (3) Å^3; $Z = 2$; $D_c = 1.40$ g cm^{-3}; $F(000) = 1100$; Mo Kα radiation ($\bar{\lambda} = 0.71069$ Å); μ(Mo Kα) = 7.25 cm^{-1}; space group $P\bar{1}$ (from structural analysis).

Intensity measurements were made at room-temperature on a roughly prismatic crystal, of approximate dimensions 0.21 × 0.26 × 0.48 mm, mounted with its c axis colinear with ϕ axis of the diffractometer. Niobium-filtered Mo Kα radiation and the moving counter–moving crystal scan technique were used, the drive speed being related to the number of counts on the peak (lowest speed 2.5°/min). For intensities and background the "five-points" technique[12] was used. Despite the reasonably large dimensions the crystal diffracted weakly, showing a significant fall–off of intensities at higher angles. Because of this fact, only a limited intensity data set could be collected, 5836 independent reflections over the range $5.0° < 2\theta < 44.0°$; of these, only 1942 reflections were considered as "observed" having $I \geq \sigma(I)$ and were used in the crystal analysis. Moreover, the intensity of a standard reflection, monitored every 20 measurements as a general check on crystal and electronic stability, exhibited an average decline of ~40% during the time required to collect data. A correction for this crystal decay, which was due to decomposition caused by X-rays, was applied by means of a computer program which uses the intensity of the standard reflection as an internal scaling for the data set. Corrections to the structure amplitudes were made for Lorentz and polarization factors, while the absorption effects were disregarded in view of the very low absorbance of the sample ($\mu r = 0.08$). Data were placed on an absolute scale first by correlating observed and calculated structure amplitudes and then by determining the scale factor for the F_0 values as a parameter in th least-square refinement.

Solution and Refinement of the Structure. The structure was solved by a combination of direct methods and the heavy-atom technique. Refinement was carried out by means of full-matrix least squares. Because of the paucity of data, isotropic thermal parameters for all atoms were used, except for the cobalt atoms, which were treated anisotropically. In this way the ratio observations:parameters was 6.6:1, a rather low value, but at the limit of acceptability for structure analyses. The function minimized was $\sum w|\Delta F^2|$; unit weights were used at first, while in the last cycles the weighting scheme $w = 1/\sigma^2(F_o^2 + 0.005F_o^2)$, based on counting statistics, was assumed. The final R's, ignoring the contribution of seven reflections with large values of $|F_o - F_c|$ were $R = 0.109$ ($R = \sum||F_o| - |F_c||/\sum|F_o|$) and $R_w = 0.111$ ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$). Attempts to refine beyond this point resulted in increasing distortion of the molecular geometry and unlikely thermal parameters which were related to the low percentage of observed reflections. As a final check of the correctness of the structure a difference Fourier synthesis was calculated and found to contain no feature of chemical significance. The largest peak was of height 0.48 e Å^{-3} and was close to that of Co(1). The shifts on the last cycle of refinement were less than 0.4σ for all parameters.

Positional and thermal parameters are given in Table IV. A list of observed and calculated structure factors has been deposited as supplementary material. Atomic factors were taken from Cromer and Mann.[13] All computations were performed with use of the SHELX-76 system of programs.[14]

Results and Discussion

$[M(NMA)_2]$ and $AsPh_4[M(NMA)_3]$ Complexes. The reaction of nitromalonaldehyde anion (NMA) with metal(II) chloride in the molar ratio 2:1 gives the $[M(NMA)_2 \cdot nH_2O]$ [M = Zn(II), Ni(II), Cu(II), Co(II), Fe(II); n = 2–4] compounds which form the corresponding $[M(NMA)_2]$ derivatives by heating under vacuum. With a molar ratio 3:1 or higher the monomeric octahedral $[M(NMA)_3]^-$ anion of iron(II) and cobalt(II) can be obtained.

Their analytical data and other selected properties are reported in Tables I and II.

The IR spectra of the $[M(NMA)_2]$ complexes show a strong band in the 1630–1640-cm^{-1} region which can be attributed to the ν(C=O) stretching frequencies. For the free ligand (obtained as sodium salt) this band appears at 1655 cm^{-1}. In the 1500–1550 and 1300–1350-cm^{-1} regions the complexes exhibit bands due to the NO_2 group of the ligand.

In anhydrous conditions the bis(ligand) compounds are insoluble in any polar or nonpolar solvent. Therefore information on the existence in solution of monomeric or polymeric species by molecular weight and electronic spectral measurements cannot be obtained. In solid state at 25 °C the magnetic moments of 3.14, 4.90, and 5.40 μ_B for nickel, cobalt, and iron complexes, respectively, are characteristic of octahedral species and analogous to those reported for the corre-

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Table I. Some Properties and Analytical Data for the Nitromalonaldehyde Complexes

compd	color	mp,[a] °C	Λ_M, Ω^{-1} M^{-1} cm^2	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	μ_{eff},[d] μ_B	ν(CO),[h] cm^{-1}	τ (NMA protons)
[Zn(NMA)$_2$]	pink	235		24.22	24.09	1.36	1.45	9.42	9.39	diam	1640 s	0.40[i]
[Cu(NMA)$_2$]	blue	191		24.38	24.26	1.35	1.39	9.48	9.42	1.79	1632 s, 1621 s	
[Ni(NMA)$_2$]	green	>270		24.78	24.66	1.39	1.49	9.63	9.52	3.14	1630 s	
[Co(NMA)$_2$]	pink	>270		24.76	24.61	1.38	1.54	9.62	9.47	4.90	1630 s	
AsPh$_4$[Co(NMA)$_3$]	pink	198	55.4[b]	50.01	50.33	3.29	3.25	5.32	5.16	4.95, (4.91)[e]	1636 s	
[Fe(NMA)$_2$]	red-brown	225		25.02	25.12	1.40	1.61	9.73	9.47	5.40	1631 s	
AsPh$_4$[Fe(NMA)$_3$]	red	189	60.5[b]	50.32	50.42	3.30	3.39	5.34	5.19	5.29, (5.32)[e]	1629 s	
[Pd(NMA)$_2$]	yellow	212		21.28	20.60	1.19	1.14	8.24	8.05	diam	1667 s, 1606 s	0.60 br[j]
K[PtCl$_2$(NMA)][f]	yellow-orange	149	108[c]	8.55	8.50	0.47	0.89	3.32	3.05	diam	1597 s	0.57 t (40 Hz)[i]
AsPh$_4$[PtCl$_2$(NMA)][g]	yellow	164	114[c]	42.42	42.42	2.90	2.99	1.83	1.65	diam	1600 s	0.55 t (40 Hz)[i]

[a] Determined in capillaries and uncorrected. [b] Molar conductances were determined in 10^{-3} M solution of nitromethane at 25 °C. [c] Molar conductance determined in 10^{-3} M solution of acetone at 25 °C. [d] In solid state at 25 °C. [e] In CH_2Cl_2 solution at 37 °C. [f] % Cl: calcd, 16.86; found, 16.70. [g] % Cl: calcd, 9.26; found, 9.37. [h] In KBr pellets. [i] In $(CD_3)_2CO$. [j] In $(CD_3)_2SO$.

Table II. Electronic Absorption Spectra of the Complexes and of the Adducts

compd	medium	λ_{max}, nm (ϵ)
[Cu(NMA)$_2$]	Nujol	675, 783 sh
[Ni(NMA)$_2$]	Nujol	648
[Ni(NMA)$_2$(H$_2$O)$_4$]	acetone	475 sh, 640 (6.7), 740 sh
[Ni(NMA)$_2$(py)$_2$]	acetone[a]	500 (6.9), 589 (13.8)
	CH_2Cl_2	475 sh, 498 sh, 509 (49.8), 535 (40.8)
AsPh$_4$[Co(NMA)$_3$]	Nujol	470 sh, 510, 540
[Co(NMA)$_2$]	Nujol	475 sh, 506, 543
[Co(NMA)$_2$(H$_2$O)$_3$]	acetone	470 (28.5), 493 (36.5), 510 (36.1), 545 sh
[Co(NMA)$_2$(py)$_2$]	acetone[a]	470 sh, 500 (64.9), 533 sh
	CH_2Cl_2	425 (2.3×10^3), 438 sh, 488 (1.5×10^3), 753 (28)
AsPh$_4$[Fe(NMA)$_3$]	Nujol	430, 490, 760
[Fe(NMA)$_2$]	Nujol	428, 485, 750
[Fe(NMA)$_2$(H$_2$O)$_2$]	acetone	427 (1.4×10^3), 755 (31)

[a] Containing excess of pyridine.

sponding acetylacetonato complexes.[15-17] The reflectance spectra of the cobalt and iron derivatives are very similar to those of the octahedral tris(ligand) AsPh$_4$[M(NMA)$_3$] complexes while a good similarity between the spectrum (λ_{max} = 648 nm) of the [Ni(NMA)$_2$] compound and that of the octahedral Ni(acac)$_2$]$_3$[15a,18] chelate is observed.

On this basis one can suggest that the nitromalonaldehyde gives rise to polymeric structures by sharing of oxygen atoms forming an octahedral environment for the central atom as in the acetylacetonate derivatives.

Surprisingly, NMA with cobalt(II) and iron(II) also forms monomeric tris(ligand) AsPh$_4$[M(NMA)$_3$] compounds which are 1:1 electrolytes[19] and air stable both as solids and in solution. Some of their properties and their electronic spectra are reported in Tables I and II. The magnetic moments indicate high-spin configurations. Since no spectral changes were observed in the concentration range 10^{-2}–10^{-4} M, the dissociation of the complexes to give penta- or tetracoordinate species can be excluded. This behavior is peculiar if one takes into account that no β-dicarbonyl complex of nickel(II), cobalt(II), and iron(II) studied has ever been obtained as a nomoneric tris(ligand)metal(II) derivative. Furthermore, while the acetylacetonates form polymeric structures,[17,20,21] by replacement of both dimethyl groups with larger groups, a partial or complete dissociation occurs: in the case of the very bulky *tert*-butyl group, the monomeric tetracoordinated molecules are obtained exclusively. In our case therefore it seems reasonable to attribute the formation of monomeric octahedral tris(ligand) complexes as well as the formation of the polymeric [M(NMA)$_2$] species to steric factors of the ligand in which two hydrogen atoms replace the methyl groups of acetylacetone. However, the electron-withdrawing capacity of the NO_2 group in the NMA, which decreases the basicity of the coordinated oxygen atoms, may not be underestimated. In fact, using hexafluoroacetylacetone (hfac) having steric requirements like acac and electronic properties like NMA, we were able to obtain the (hfac)$_3$Co^{II} complex. Taking into account also the studies on the influence of electronic factors on the relative stabilities of the low-spin and high-spin forms of [NiL$_2$] (L = β-dicarbonyl),[22] it can be concluded that the presence of an electron-withdrawing group on a ligand not containing bulky groups allows one to obtain the monomeric octahedral tris(β-dicarbonyl) complexes together with the well-known polymeric [ML$_2$] species.

Platinum and Palladium Complexes. Nitromalonaldehyde reacts in aqueous solution with K$_2$PtCl$_4$ to give only the [PtCl$_2$(NMA)]$^-$ anion which was obtained as K$^+$ and AsPh$_4^+$ salts. Under the same conditions, K$_2$PdCl$_4$ gives [Pd(NMA)$_2$]. The conductivity values of the Y[PtCl$_2$(NMA)] (Y = K$^+$, AsPh$_4^+$) complexes (Table I) are in agreement with 1:1 electrolytes, and their IR spectra show intense bands at 1595 and 1600 cm^{-1}, respectively, attributed to the ν(C=O) stretching frequencies.[23] Furthermore, in the Pt–Cl region two bands at 345 and 366 cm^{-1} (Y = K$^+$) and at 344 and 365 cm^{-1} (Y = AsPh$_4^+$) are present, indicating that the two chlorides are in cis position.[24] Finally, the NMR spectra show a triplet at τ 0.55 (Y = AsPh$_4^+$) or 0.57 (Y = K$^+$) with a coupling constant of 40 Hz attributed to the β-proton of the coordinated nitromalonaldehyde.

The reported reaction of acetylacetone with the chloroplatinate ion in alkaline solution gives, in addition to the K[PtCl$_2$(acac)] complex, [Pt(acac)$_2$], K[PtCl(acac)$_2$], K[Pt(acac)$_3$] and Na$_2$[PtCl$_2$(acac)$_2$]·5H$_2$O derivatives.[25-27] A

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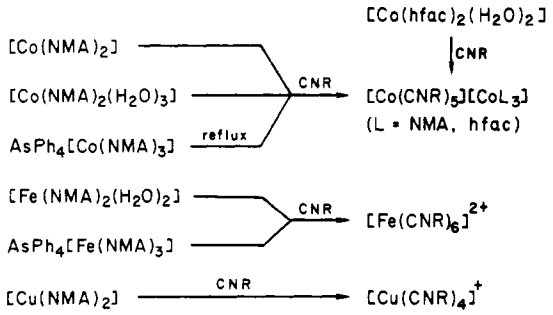
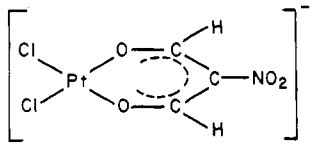
Scheme I



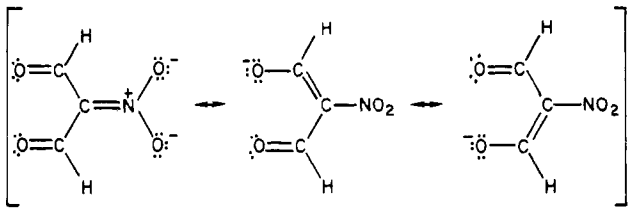
crystal structure determination has shown that the K[PtCl(acac)$_2$] derivative contains one carbon-bonded and one oxygen-bonded ligand.[26]

In our case only K[PtCl$_2$(NMA)] was obtained, and on the basis of the stoichiometry of the compound and its infrared properties, a structure of the type I with platinum–oxygen bonds can be proposed.



I

In fact, taking into account that in the oxygen-bonded acac complex the carbon-oxygen bond order is about 1.5 while in the carbon-bonded structure the carbonyl groups are more nearly like organic carbonyl groups with a bond order of 2,[27] the lower ν(CO) (55 cm^{-1}) for the [PtCl$_2$(NMA)]$^-$ derivatives compared to the free ligand suggests that only a oxygen-bonded nitromalonaldehyde is present. This is also in agreement with the extended conjugation present in ligand II, which can be maintained only when coordination to the metal center occurs through the oxygen atom(s).



II

Reactivity with Isocyanides. The results are summarized in Scheme I.

The bis(nitromalonaldehyde)cobalt(II) complex, [Co(NMA)$_2$], and the adduct [Co(NMA)$_2$(H$_2$O)$_3$] react with isocyanides to give [Co(CNR)$_5$][Co(NMA)$_3$] [R = 4-CH$_3$C$_6$H$_4$, 4-CH$_3$OC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 4-ClC$_6$H$_4$) complexes. The reduction of the cobalt atom producing [Co(CNR)$_5$]$^+$ species is not quantitative since the tris(ligand) [Co(NMA)$_3$]$^-$ anion, formed during the course of the reaction, reacts very slowly with isocyanides. Therefore from the reaction mixture the [Co(CNR)$_5$][Co(NMA)$_3$] derivatives can be obtained as crystalline products. In the same way also the hexafluoroacetylacetonate (hfac) complex [Co(hfac)$_2$(H$_2$O)$_2$] reacts with isocyanides to give the [Co(CNR)$_5$][Co(hfac)$_3$] complexes (R = 4-CH$_3$C$_6$H$_4$, 4-CH$_3$OC$_6$H$_4$).

On the contrary no evidence of the formation of the pentakis(isocyanides) [Co(CNR)$_5$]$^+$ was obtained by the reaction

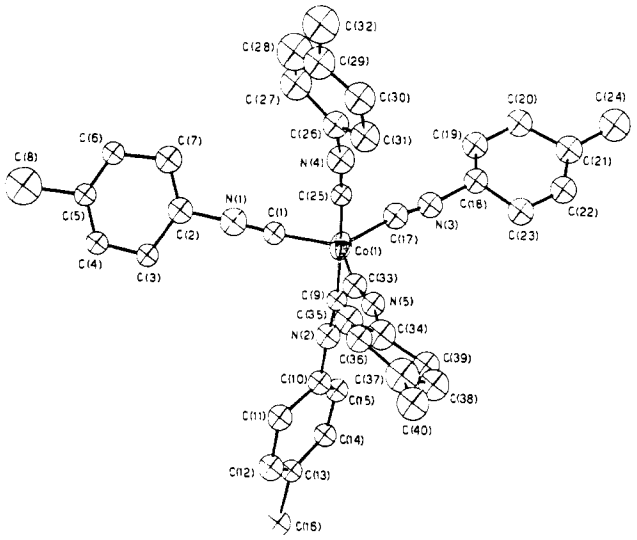


Figure 1. ORTEP plot showing the five-coordinated Co(I) environment in the cation (ellipsoids of 30% probability are shown).

of the acetylacetone complexes [Co(acac)$_2$]$_n$ and [Co(acac)$_2$(H$_2$O)$_2$] with isocyanides. It follows from these data that only with ligands containing a good electron-withdrawing group (i.e., NO_2 or CF_3) can the reduction of the cobalt(II) chelates take place.

Reaction of the iron nitromalonaldehyde chelates with CNR produces the hexakis(isocyanide)iron(II) compounds while in the same reaction the copper is reduced to form tetrakis(isocyanide)copper(I) derivatives.

The hexakis(aryl isocyanide)iron(II) complexes are uncommon, and the previously reported ones[28] were prepared by the reaction of solid iron(II) perchlorate with isocyanides without solvent. With the nitromalonaldehyde derivative a new method is proposed as well as for the [Cu(CNR)$_4$]ClO$_4$ compounds previously obtained by reaction of CuCl with isocyanides in alcohol.[29]

Good analytical data have been obtained (Table III) after crystallization of the products. For the [Co(CNR)$_5$][Co(NMA)$_3$] and the [Co(CNR)$_5$][Co(hfac)$_3$] complexes the conductivity values are in agreement with those reported for 1:1 electrolytes containing B(C$_6$H$_5$)$_4^-$ as counterion. The IR spectra of these compounds, besides the band at 1636 cm^{-1} due to the ν(CO) of [Co(NMA)$_3$]$^-$ anion, show two intense bands in the ν(CN) stretching region at 2145–2150 cm^{-1} (solid state) and at 2107–2111 cm^{-1} (CH$_2$Cl$_2$ solution) attributed to the [Co(CNR)$_5$]$^+$ cation. A similar IR spectrum is reported for the [Co(C$_6$H$_5$NC)$_5$]ClO$_4$ complex previously obtained in a different way.[30] A strong infrared band at 2193 cm^{-1} and a shoulder at 2238 cm^{-1} is present in the spectrum of the [Fe(CNR)$_6$](ClO$_4$)$_2$ derivative.

In the solid state, the [Cu(4-CH$_3$C$_6$H$_4$NC)$_4$]ClO$_4$ complex shows a band at 2168 cm^{-1} while in CH$_2$Cl$_2$ solution two bands at 2172 and 2156 cm^{-1} are present. Furthermore in the methyl region of the NMR spectrum two resonance lines are present at τ 7.58, and 7.83. The line at τ 7.83 increases with time while that at τ 7.58 decreases, respectively (and their final intensity ratio is 3:2). Since the instability in solution of [Cu(CNR)$_4$]$^+$ complexes is known,[29] the formation of [Cu(CNR)$_3$]$^+$ or [Cu(CNR)$_2$]$^+$ species may be invoked to explain the reported data.

Crystallographic Analysis. From a structural point of view the significance of the title compound is due to the presence

(26) B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *Nature (London)*, **195**, 1278 (1962).
(27) (a) J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965); (b) D. Gibson, *Coord. Chem. Rev.*, **4**, 225 (1969).
(28) F. Bonati and G. Minghetti, *J. Organomet. Chem.*, **22**, 195 (1970).
(29) F. Klages, K. Moenkemeyer, and R. Heinle, *Chem. Ber.*, **85**, 109. (1952).
(30) F. A. Cotton, and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

Table III. Analytical and Spectroscopic Data for Isocyanide Complexes

compd	color	mp, °C	Λ_M,[a] cm^2 Ω^{-1} M^{-1}	% C		% H		% N		ν(CN) in CH_2Cl_2 (in KBr), cm^{-1}	τ (methyl protons)
				calcd	found	calcd	found	calcd	found		
$[Co(4\text{-}CH_3C_6H_4NC)_3][Co(NMA)_3]$	orange	170	14.60, 48.2[b]	55.95	55.63	3.93	4.12	10.66	10.56	2150 s, 2110 s, 2038 sh (2147 s, 2102 s, 2030 sh)	7.72 s
$[Co(4\text{-}CH_3OC_6H_4NC)_3][Co(NMA)_3]$	orange	138	14.67	52.00	52.44	3.65	3.79	9.90	9.88	2146 s, 2107 s, 2040 sh (2134 s, 2110 s, 2038 sh)	6.19 s
$[Co(4\text{-}NO_2C_6H_4NC)_3][Co(NMA)_3]$	red-brown	168	13.56	43.79	43.82	2.17	2.40	15.09	15.23	2150 s, 2108 s (2153 s, 2116 s)	
$[Co(4\text{-}ClC_6H_4NC)_3][Co(NMA)_3]$[c]	yellow-orange	180	14.04	45.48	45.48	2.27	2.39	9.71	9.48	2145 s, 2110 s (2148 s, 2108 s)	
$[Co(4\text{-}CH_3C_6H_4NC)_3][Co(tifac)_3]$	orange	144	14.46	49.86	49.86	2.89	2.98	5.29	5.30	2150 s, 2112 s, 2038 sh (2138 s, 2104 s, 2030 sh)	8.01 s
$[Co(4\text{-}CH_3OC_6H_4NC)_3][Co(hfac)_3]$	orange	137	14.52	47.02	46.78	2.73	2.83	4.99	4.92	2147 s, 2109 s (2140 s, 2104 s)	6.60 s
$[Fe(4\text{-}CH_3C_6H_4NC)_6][ClO_4)_2$[d]	yellow	174	46.5	60.20	61.25	4.42	4.80	8.78	8.81	2238 sh, 2193 s (2240 sh, 2195 s)	7.60 s
$[Cu(4\text{-}CH_3C_6H_4NC)_4]ClO_4$[e]	white	170	25.43	60.85	59.81	4.47	4.87	8.87	8.52	2172 s, 2156 s (2168 s)	7.58 s, 7.83 s

[a] In 10^{-3} M nitrobenzene solutions at 25 °C. [b] In 10^{-3} M nitromethane solution at 25 °C. [c] % Cl: calcd, 15.36; found, 15.92. [d] % Cl: calcd, 7.40; found, 7.75. [e] % Cl: calcd, 5.61; found, 5.36.

Table IV. Fractional Atomic Coordinates ($\times 10^4$ for Co; $\times 10^3$ for O, N, and C) and Thermal Parameters ($\times 10^3$ for Co; $\times 10^2$ for O, N, and C)

atom	x	y	z	U, $Å^2$
Co(1)	4130 (6)	2933 (4)	8158 (7)	
Co(2)	1051 (6)	2350 (4)	2237 (7)	
O(1)	−42 (2)	189 (2)	194 (3)	9 (1)
O(2)	−283 (4)	135 (3)	−93 (5)	19 (2)
O(3)	−216 (5)	191 (3)	−188 (6)	19 (2)
O(4)	56 (3)	249 (2)	59 (4)	11 (1)
O(5)	152 (3)	226 (2)	390 (4)	12 (1)
O(6)	140 (3)	373 (2)	703 (4)	14 (1)
O(7)	90 (3)	476 (3)	640 (3)	14 (1)
O(8)	97 (2)	358 (2)	315 (3)	8 (1)
O(9)	109 (2)	109 (2)	128 (3)	9 (1)
O(10)	385 (4)	155 (3)	35 (4)	18 (2)
O(11)	291 (3)	24 (3)	−43 (4)	15 (2)
O(12)	249 (2)	273 (2)	239 (3)	10 (1)
N(1)	421 (3)	424 (2)	701 (3)	9 (1)
N(2)	474 (3)	182 (2)	622 (3)	7 (1)
N(3)	592 (3)	281 (2)	1029 (4)	7 (1)
N(4)	338 (3)	410 (2)	981 (4)	9 (1)
N(5)	234 (3)	171 (2)	752 (3)	7 (1)
N(6)	−216 (6)	167 (4)	−111 (6)	16 (2)
N(7)	124 (3)	407 (3)	627 (4)	11 (2)
N(8)	318 (4)	96 (4)	5 (5)	12 (2)
C(1)	415 (3)	371 (3)	740 (4)	6 (1)
C(2)	417 (4)	288 (3)	643 (5)	8 (1)
C(3)	363 (3)	452 (3)	508 (4)	6 (1)
C(4)	362 (3)	515 (3)	455 (4)	6 (1)
C(5)	407 (3)	596 (3)	530 (5)	6 (1)
C(6)	448 (3)	632 (2)	653 (4)	6 (1)
C(7)	459 (4)	574 (3)	723 (5)	8 (2)
C(8)	398 (5)	663 (4)	455 (6)	16 (3)
C(9)	451 (3)	223 (2)	705 (4)	5 (1)
C(10)	493 (4)	125 (3)	520 (4)	7 (1)
C(11)	413 (3)	108 (3)	393 (4)	8 (1)
C(12)	423 (4)	47 (3)	284 (4)	8 (1)
C(13)	522 (3)	30 (2)	309 (4)	6 (1)
C(14)	596 (3)	54 (2)	428 (4)	6 (1)
C(15)	587 (4)	105 (3)	531 (4)	6 (1)
C(16)	533 (3)	−31 (3)	188 (4)	8 (1)
C(17)	535 (4)	293 (3)	956 (5)	8 (2)
C(18)	660 (4)	278 (3)	1143 (5)	7 (1)
C(19)	748 (4)	334 (3)	1211 (5)	8 (1)
C(20)	809 (4)	329 (3)	1319 (5)	8 (1)
C(21)	793 (4)	246 (3)	1343 (5)	9 (1)
C(22)	704 (4)	189 (3)	1257 (5)	8 (1)
C(23)	637 (4)	193 (3)	1152 (5)	8 (1)
C(24)	872 (4)	244 (3)	1458 (5)	12 (2)
C(25)	367 (3)	361 (3)	914 (4)	5 (1)
C(26)	271 (4)	459 (3)	1041 (4)	8 (1)
C(27)	286 (4)	553 (4)	1059 (5)	12 (2)
C(28)	221 (6)	594 (4)	1118 (6)	16 (3)
C(29)	153 (5)	552 (4)	1135 (5)	12 (2)
C(30)	141 (4)	466 (4)	1127 (5)	12 (2)
C(31)	202 (4)	412 (3)	1063 (5)	11 (2)
C(32)	83 (5)	600 (4)	1210 (6)	16 (2)
C(33)	300 (4)	218 (3)	760 (4)	7 (1)
C(34)	128 (5)	114 (4)	705 (5)	10 (2)
C(35)	45 (5)	159 (3)	684 (5)	10 (2)
C(36)	−45 (4)	118 (3)	664 (4)	8 (2)
C(37)	−60 (5)	26 (4)	658 (6)	14 (2)
C(38)	23 (5)	−10 (4)	687 (6)	11 (2)
C(39)	124 (4)	30 (3)	714 (5)	8 (1)
C(40)	−169 (5)	−29 (3)	620 (5)	12 (2)
C(41)	−124 (4)	165 (3)	89 (5)	8 (2)
C(42)	−116 (4)	197 (3)	8 (5)	9 (2)
C(43)	−38 (4)	226 (3)	−21 (4)	6 (1)
C(44)	160 (4)	281 (4)	495 (5)	11 (2)
C(45)	122 (4)	359 (3)	506 (5)	9 (2)
C(46)	101 (3)	400 (3)	420 (4)	7 (1)
C(47)	172 (4)	85 (3)	72 (5)	8 (2)
C(48)	250 (4)	139 (3)	82 (4)	8 (1)
C(49)	284 (4)	229 (3)	160 (5)	9 (2)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	80 (6)	76 (5)	91 (6)	44 (5)	50 (5)	47 (5)
Co(2)	80 (7)	89 (6)	85 (6)	41 (5)	37 (5)	45 (5)

Table V. Selected Bond Lengths (Å) and Angles (Deg)

(i) In the Cation

Co(1)-C(1)	1.82 (5)	C(1)-N(1)	1.14 (7)	N(1)-C(2)	1.45 (8)
Co(1)-C(9)	1.74 (5)	C(9)-N(2)	1.18 (6)	N(2)-C(10)	1.42 (6)
Co(1)-C(17)	1.98 (5)	C(17)-N(3)	1.07 (7)	N(3)-C(18)	1.42 (7)
Co(1)-C(25)	1.70 (5)	C(25)-N(4)	1.16 (6)	N(4)-C(26)	1.52 (7)
Co(1)-C(33)	1.75 (5)	C(33)-N(5)	1.14 (7)	N(5)-C(34)	1.53 (7)
$C(sp^2)$-$C(sp^2)$	1.40 (8)[a]	$C(sp^2)$-$C(sp^3)$	1.59 (8)[a]		

C(1)-Co(1)-C(9)	88 (2)	C(9)-Co(1)-C(25)	175 (3)
C(1)-Co(1)-C(17)	121 (2)	C(9)-Co(1)-C(33)	90 (2)
C(1)-Co(1)-C(25)	90 (2)	C(17)-Co(1)-C(25)	93 (2)
C(1)-Co(1)-C(33)	118 (2)	C(17)-Co(1)-C(33)	121 (3)
C(9)-Co(1)-C(17)	91 (2)	C(25)-Co(1)-C(33)	87 (2)
Co(1)-C(1)-N(1)	175 (4)	C(1)-N(1)-C(2)	174 (5)
Co(1)-C(9)-N(2)	172 (4)	C(9)-N(2)-C(10)	174 (5)
Co(1)-C(17)-N(3)	169 (5)	C(17)-N(3)-C(18)	167 (5)
Co(1)-C(25)-N(4)	178 (5)	C(25)-N(4)-C(26)	164 (5)
Co(1)-C(33)-N(5)	164 (5)	C(33)-N(5)-C(34)	162 (5)
N-C-C	116 (5)[a]	$C(sp^2)$-$C(sp^2)$-$C(sp^3)$	119 (5)[a]
$C(sp^2)$-$C(sp^2)$-$C(sp^2)$	120 (5)[a]		

(ii) In the Anion

Co(2)-O(1)	2.05 (4)	O(1)-C(41)	1.32 (5)	C(41)-C(42)	1.31 (9)
Co(2)-O(4)	1.98 (5)	O(4)-C(43)	1.30 (6)	C(43)-C(42)	1.38 (9)
Co(2)-O(5)	1.96 (4)	O(5)-C(44)	1.26 (7)	C(44)-C(45)	1.44 (8)
Co(2)-O(8)	2.01 (3)	O(8)-C(46)	1.22 (6)	C(46)-C(45)	1.38 (8)
Co(2)-O(9)	2.05 (3)	O(9)-C(47)	1.31 (7)	C(47)-C(48)	1.34 (8)
Co(2)-O(12)	2.03 (4)	O(12)-C(49)	1.28 (7)	C(49)-C(48)	1.41 (6)
C-N	1.53 (8)[a]	N-O	1.17 (7)[a]		

O(1)-Co(2)-O(4)	90 (2)	O(4)-Co(2)-O(12)	87 (2)
O(1)-Co(2)-O(5)	90 (2)	O(5)-Co(2)-O(8)	86 (2)
O(1)-Co(2)-O(8)	92 (1)	O(5)-Co(2)-O(9)	95 (2)
O(1)-Co(2)-O(9)	87 (1)	O(5)-Co(2)-O(12)	94 (2)
O(1)-Co(2)-O(12)	175 (1)	O(8)-Co(2)-O(9)	179 (1)
O(4)-Co(2)-O(5)	177 (2)	O(8)-Co(2)-O(12)	92 (1)
O(4)-Co(2)-O(8)	92 (2)	O(9)-Co(2)-O(12)	89 (1)
O(4)-Co(2)-O(9)	87 (2)	Co(2)-O(8)-C(46)	135 (3)
Co(2)-O(1)-C(41)	129 (3)	Co(2)-O(9)-C(47)	126 (3)
Co(2)-O(4)-C(43)	125 (4)	Co(2)-O(12)-C(49)	121 (3)
Co(2)-O(5)-C(44)	130 (4)	C-C-C	130 (6)[a]
O-C-C	121 (5)[a]	C-N-O	112 (6)[a]
C-C-N	114 (5)[a]	O-N-O	133 (6)[a]

[a] Mean value.

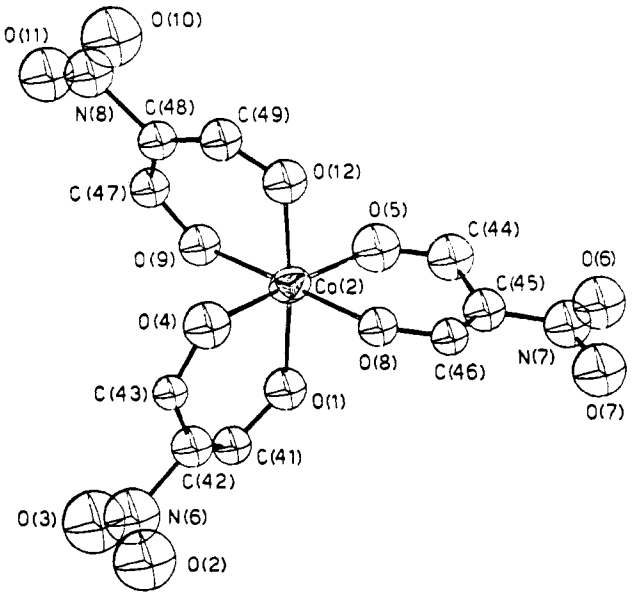


Figure 2. ORTEP plot showing the hexacoordinated Co(II) environment in the anion (ellipsoids of 30% probability are shown).

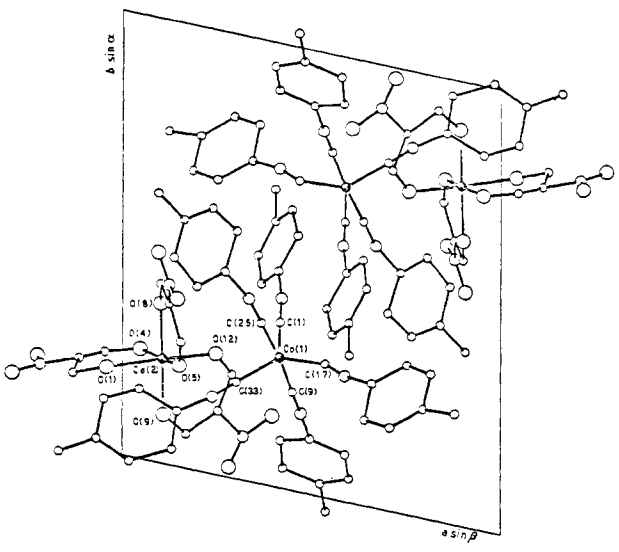


Figure 3. Projection of the structure on a plane perpendicular to [001] showing the molecular packing.

of two nonequivalent cobalt atoms which are different in environment and in formal oxidation state. In the cation the coordination polyhedron has the shape of a trigonal bipyramid with the five isocyanide ligands bound to cobalt(I) (Figure 1), , while in the anion the coordination geometry around cobalt(II) is octahedral and involves the three nitromalonic dialdehyde anions (Figure 2).

Table V lists selected bond lengths and angles. Individual values within the ligand molecules have not been reported as the light atoms in the structure exhibit high thermal motion

and the resultant high standard deviations in the structural parameters limit conclusions and discussion based on differences in these parameters. However, despite the high R value and the abnormally high percentage of unobserved reflections resulting from the poor quality of the crystal, the atom connectivities are unequivocally established and the overall gross geometry is undoubtedly correct.

Concerning the cation, a survey of X-ray structural determinations of cobalt(I) compounds has revealed the persistence of five-coordination for the metal, with trigonal bipyramidal appearing to be the preferred arrangement compared with square pyramidal.[31] Incidentally, it can be observed that, of the 14 Co(I) compounds, 11 have phosphines bound to metal. In the present compound the values of the bond angles at Co(I) indicate that the coordination polyhedron is a slightly distorted trigonal bipyramid; the largest deviation from the expected values for an ideal geometry is observed in the axial C(9)–Co(1)–C(25) angle (175°). The cobalt atom is coplanar with the three equatorial carbon atoms C(1), C(17), and C(33), and this fact allows the equatorial angles to attain values close to 120°. The six angles between the apical and equatorial bonds range from 87 to 93°. The Co–C bond lengths all show a strong metal-to-ligand π back-donation which results in an increase of the Co–C bond order. Some differences have been observed in these bonds, with the two shortest values involving the apical bonds, but little or no significance can be attached to this fact in view of the rather large standard deviations. However, the mean value of 1.80 Å compares well with those observed in the other trigonal-bipyramidal cobalt(I) derivatives involving isocyanide ligands: 1.84, 1.88, and 1.88 Å in pentakis(methyl isocyanide)cobalt(I) perchlorate;[31a] 1.78, 1.81, and 1.81 Å in tris(4-nitrophenyl isocyanide)bis(diethyl phenylphosphonite)cobalt(I) perchlorate;[31b] 1.83 and 1.85 Å in tris(*p*-fluorophenyl isocyanide)bis(trimethyl phosphite)cobalt(I) tetrafluoroborate.[31n] In the present compound some of the Co–C–N and C–N–C angles show a large deviation from linearity.

In the anion, the cobalt atom is hexacoordinated by the oxygen atoms belonging to three NMA molecules which behave as bidentate chelating ligands. The six Co–O bond lengths are not significantly different, the range being 1.96–2.05 Å, with a mean value of 2.01 Å which compares fairly well with those found in other (acetylacetonato)cobalt(II) derivatives and involving nonbridging oxygen atoms (e.g., 2.05 and 2.06 Å in $[Co(acac)_2]\cdot 2H_2O$,[8] 2.04 Å (average) in $[Co(acac)_2]_4$, 2.02 Å (average) in $[Co(acac)_2]_2\cdot 2H_2O$,[32] and 2.03 Å (average) in $[Co(acac)_2]_3\cdot H_2O$[33]). Bond angles in the cobalt environment show only small departures from the ideal octahedral values as they are in the range 86–95° (cis angles) and 175–179° (trans angles). The three chelate rings are similar in bond lengths, angles, and deviations from the mean least-squares planes. Comparing bond distances and angles found in the present compound with the corresponding average values given by Lingafelter and Braun[34] for some acetylacetonate chelate structures, it can be seen that the agreement is fairly good for the distances [C–O = 1.28 Å (average) (present compound) vs. 1.274 Å (literature); C–C = 1.38 Å vs. 1.390 Å), while it is less satisfactory for the angles (O–C–C = 121° vs. 125.3°; C–C–C = 130° vs. 124.0°]. The chelate rings are roughly planar, even though none of them can be considered as strictly planar on the basis of χ^2 at 95% for 3 degrees of freedom. In each ring the cobalt atom lies always at the opposite site with respect to the coordinated oxygen atoms. The nitro group is not coplanar with the six-membered ring to which it is attached, the dihedral angle between the two parts ranging from 7 to 10°.

As shown in Figure 3 packing is due to van der Waals interactions. The shortest cation–anion intermolecular contacts are in the range 3.20–3.30 Å, while the cation–cation and the anion–anion contacts are all longer than 3.40 Å.

Conclusions

With the nitromalonaldehyde ligand the syntheses of the first monomeric tris(β-dicarbonyl)metal(II) complexes of cobalt(II) and iron(II) have been achieved, and the results have been tentatively explained on the basis of both steric and electronic properties of the dialdehyde ligand compared with various substituted acetylacetonates. Beside these types of complexes, the bis(nitromalonaldehyde)metal(II) derivatives were obtained, and, like other dicarbonyls, a polymeric structure may be proposed. The reaction of the chloroplatinite anion with nitromalonaldehyde gives only the $Y[PtCl_2(NMA)]$ derivative which contains an oxygen-bonded ligand.

Reaction of the cobalt(II) derivatives with π-acceptor ligands such as isocyanides proceeds with partial reduction to the cobalt(I) to give $[Co(CNR)_5][Co(NMA)_3]$ as the final product. The crystal structure of the 4-tolyl isocyanide derivative shows that, in the cation, the coordination polyhedron has the shape of a trigonal bipyramid with the five isocyanide ligands bound to the cobalt(I), while in the anion the coordination geometry around cobalt(II) is octahedral and involves the three nitromalonaldehyde molecules. Finally, $[Fe(CNR)_6]^{2+}$ and $[Cu(CNR)_4]^{+}$ cations have been prepared by the reaction of isocyanides with the iron(II) and copper(II) chelates.

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Registry No. $Zn(NMA)_2$, 77744-62-8; $Cu(NMA)_2$, 77744-63-9; $Ni(NMA)_2$, 77744-61-7; $Co(NMA)_2$, 77773-59-2; $Fe(NMA)_2$, 77773-61-6; $Pd(NMA)_2$, 77744-64-0; $Ni(NMA)_2(py)_2$, 77744-65-1; $Co(NMA)_2(py)_2$, 77744-66-2; $Zn(NMA)_2(py)_2$, 77744-67-3; $AsPh_4[Co(NMA)_3]$, 77773-62-7; $AsPh_4[Fe(NMA)_3]$, 77744-69-5; $K[PtCl_2(NMA)]$, 77744-70-8; $AsPh_4[PtCl_2(NMA)]$, 77744-72-0; $[Co(4\text{-}CH_3C_6H_4NC)_5][Co(NMA)_3]$, 77773-63-8; $[Co(4\text{-}CH_3OC_6H_4NC)_5][Co(NMA)_3]$, 77841-51-1; $[Co(4\text{-}NO_2C_6H_4NC)_5][Co(NMA)_3]$, 77744-75-3; $[Co(4\text{-}ClC_6H_4NC)_5][Co(NMA)_3]$, 77744-76-4; $[Co(4\text{-}CH_3C_6H_4NC)_5][Co(hfac)_3]$, 77744-77-5; $[Co(4\text{-}CH_3OC_6H_4NC)_5][Co(hfac)_3]$, 77841-52-2; $[Fe(4\text{-}CH_3C_6H_4NC)_2](ClO_4)_2$, 26201-81-0; $[Cu(4\text{-}CH_3C_6H_4NC)_4]ClO_4$, 77744-79-7; K_2PtCl_4, 10025-99-7; K_2PdCl_4, 10025-98-6; $Co(hfac)_2$, 19648-83-0.

Supplementary Material Available: A listing of structure factor amplitudes and a table of magnetic properties (24 pages). Ordering information is given on any current masthead page.

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