0.08 (1) Å for C4). The dihedral angle between the S_2C and NC_2 planes of this ligand is 7.8°. The W atom is displaced from the S_2CNC_2 plane toward the S3 atom by 0.183 (4) Å. The structure of **1** is closely related to that of its molybdenum analogue although the bond distances within the coordination sphere of **1** are consistently longer than those of the molybdenum compound.[2]

Acknowledgment. We thank Mr. G. Jamison for the VT-NMR spectra. C.G.Y. completed this work during a sabbatical at the University of North Carolina, Chapel Hill, NC; the hospitality of that institution and the support and encouragement of Prof. J. L. Templeton and his group are gratefully acknowledged. We thank the Australian Research Council for financial support. The structure was determined in the Molecular Structure Laboratory at the University of Arizona.

Supplementary Material Available: Tables of full crystallographic data, bond distances and angles, and anisotropic thermal parameters (5 pages); a table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Rajasthan, Jaipur, India

Studies of Fluorinated 1,3-Diketones and Related Compounds. 17. Benzoic Acid Hydrazide Derivatives of 1,3-Diketones and Their Nickel Complexes. Molecular Structures of $C_6H_5C(=O)NN=C(p\text{-}FC_6H_4)CH_2C(OH)(p\text{-}FC_6H_4)$ and $[C_6H_5C(O)=NN=C(p\text{-}FC_6H_4)CH=C(O)(p\text{-}FC_6H_4)]Ni(NH_3)$

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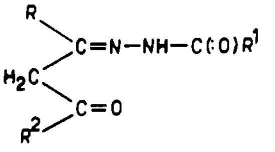
Received March 14, 1990

The synthesis and characterization of some benzoic acid derivatives of 1,3-diketones $R^1C(=O)NN=C(R)CH_2C(OH)R^2$ (R^1 = C_6H_5, p-FC_6H_4; R = CH_3, C_2H_5, p-FC_6H_4; R^2 = p-FC_6H_4, 3-CH_3-4-FC_6H_3) and their nickel complexes $[R^2C(O)=CHC(R)-=NN=C(O)R^1]Ni(NH_3)$ are reported. Spectral studies reveal that the ligands exist exclusively as cyclic tautomers corresponding to pyrazoline derivatives and undergo a ring-opening reaction on chelation with nickel. The crystal structures of $C_{22}H_{16}F_2N_2O_2$ (I) and its nickel complex $C_{22}H_{17}F_2N_3O_2Ni$ (II) are reported. The crystals of I are orthorhombic, space group *Pbca*, with a = 10.479 (4) Å, b = 16.155 (4) Å, c = 21.451 (4) Å, V = 3631.6 Å^3, Z = 8, M_r = 378.38, D_c = 1.122 g cm^{-3}, μ(Mo Kα) = 0.79 cm^{-1}, $F(000)$ = 1272, and final R = 0.074 for 1887 ($I > \sigma(I)$) of 2643 unique reflections ($2 < \theta < 25°$). The ligand exists in a cyclic tautomeric form with a planar five-membered ring corresponding to a pyrazoline derivative. The crystals of the nickel complex II are triclinic, space group $P\bar{1}$, with a = 7.553 (2) Å, b = 11.154 (3) Å, c = 12.584 (2) Å, α = 77.29 (1)°, β = 87.41 (2)°, γ = 69.93 (2)°, V = 971.1 Å^3, Z = 2, M_r = 452.11, D_c = 1.546 g cm^{-3}, μ(Mo Kα) = 10.43 cm^{-1}, $F(000)$ = 464, and final R = 0.029 for 2643 ($I > \sigma(I)$) of 3436 unique reflections ($2 < \theta < 25°$). In both the cases, λ(Mo Kα) = 0.71069 Å and T = 295 K. The crystal structure shows a square-planar geometry around the nickel atom and the tridentate bifunctional behavior of the ligand.

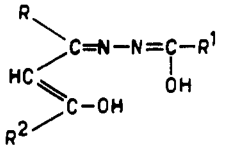
Introduction

1,3-Diketones and related compounds constitute an important class of coordination ligands, and their keto–enol tautomerism has been extensively studied.[1,2] In continuation of our earlier work on the structural studies on ligands derived from 1,3-diketones and their mode of coordination with metals,[3,4] we are now reporting the synthesis and study of some benzoic acid hydrazide derivatives of 1,3-diketones and their nickel complexes.

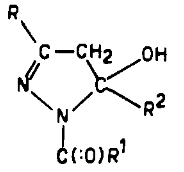
Benzoic acid hydrazide derivatives of β-dicarbonyl compounds can exist in several distinct isomeric forms, as there are several tautomeric probabilities for these compounds. A survey of the literature[5-9] reveals controversial reports on the solution tautomeric equilibria for such derivatives. Sacconi et al.,[5,6] on the basis of UV spectral studies and the mode of coordination of 1,3-diketone acylhydrazones, proposed that these exist in tautomeric forms corresponding to a hydrazone (A) and its enol form (B), with a predominance of the latter. However, Iskander et al. have reported[7] that the initial product of the condensation of benzoylacetaldehyde and aryoylhydrazines is predominantly the enolimino form rather than the ketoenamine form and the former on cyclization gives a 5-hydroxypyrazoline derivative (C). On the other hand, recent reports[8,9] on the solution tautomeric equilibria of these compounds by NMR investigations suggest that they exhibit ring–chain tautomerism involving an open-chain enehydrazine form (D) and a cyclic 5-hydroxypyrazoline form (C).



(A)



(B)



(C)

$R^2C(:O)CH:C(R)NHNHC(:O)R^1$

(D)

In view of the these observations, it was considered worthwhile to investigate, in detail, the synthesis and structural aspects of benzoic acid hydrazide derivatives of 1,3-diketones and the rearrangement they may undergo on coordination with nickel. In

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Table I. Crystallographic Data for $C_{22}H_{16}F_2N_2O_2$ (I) and $C_{22}H_{17}F_2N_3O_2Ni$ (II)

	I	II
formula (mol wt)	$C_{22}H_{16}F_2N_2O_2$ (378.38)	$C_{22}H_{17}F_2N_3O_2Ni$ (452.11)
a, Å	10.479 (4)	7.553 (2)
b, Å	16.155 (4)	11.154 (3)
c, Å	21.451 (4)	12.584 (2)
α, β, γ, deg		77.19 (1), 87.41 (2), 69.93 (2)
V, Å^3	3631.6	971.1
Z	8	2
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
d_{calcd}, g/cm^3	1.122	1.546
μ(Mo Kα), cm^{-1}	0.79	10.43
temp, °C	22	22
no. of params refined	253	339
$R(F_o)$	0.074	0.029
$R_w(F_o)$	0.097	0.036

the present paper, the solution as well as solid-state structures of these ligands and their nickel complexes are reported.

Experimental Section

Materials and Procedures. Reagents of analytical grade were used. Solvents were purified by distillation. IR spectra were recorded using a Perkin-Elmer 577 spectrophotometer in KBr pellets, ^{1}H NMR spectra by a Brucker WH-400 instrument in $CDCl_3$ and $(CD_3)_2CO$ with TMS as internal standard, and mass spectra of the ligands by a Jeol TMS-D300 instrument.

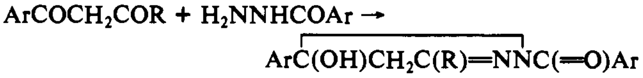
Fluorobenzene,[10] 3-methyl-4-fluorobenzene,[11] fluoroaryl ketones,[12,13] 1,3-diketones,[14] and aryolhydrazides[15,16] were prepared by literature methods.

The ligands[5] and their nickel complexes[5] were prepared by earlier reported methods; their analytical data are given in Tables II and III, respectively.

X-ray Crystallographic Studies. Suitable crystals of $C_{22}H_{16}F_2N_2O_2$ (I) and $C_{22}H_{17}F_2N_3O_2Ni$ (II) were obtained by recrystallization from ethanol solution. All relevant crystallographic information is given in Table I. The crystals were mounted on glass fibers using 5-min epoxy resin. Accurate unit cell parameters were obtained by means of least-squares analysis of 25 reflections. Intensity data on each compound was then collected by utilizing the options specified in Table SVII. An $\omega-2\theta$ scan mode was used with scan width of $0.8 + 0.35 \tan\theta$ for I and $0.7 + 0.35 \tan\theta$ for II. A variable scan speed with a maximum scan time of 1 min was used. Two standard reflections monitored ($\bar{1}63$ and $\bar{2}5\bar{1}$ for I; $1\bar{2}\bar{5}$ and $0\bar{2}\bar{6}$ for II) every 1800 showed no significant variation over the data collection. There were no crystal decays, and intensities were corrected for Lorentz and polarization factors but not for absorption. All computation was performed on a PDP 11/73 computer. Structure I was solved by direct methods (MULTAN),[17] and II, by routine heavy-atom methods and refined with SDP[18] software by a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement techniques using anisotropic thermal parameters for all non-hydrogen atoms. In the case of I, hydrogen atoms were omitted, and for II, these were located on a difference map and were refined with isotropic temperature factors. Out of 3604 and 3436 unique reflections measured for I and II, 1887 and 2643 reflections with $|F^2| > \sigma(F^2)$ were used in refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.041)^2\}^{1/2}/Lp$. The final residuals were $R = 0.074$ and 0.029 and $R_w = 0.097$ and 0.036 for I and II, respectively, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$. The atomic scattering factors were taken from ref 19.

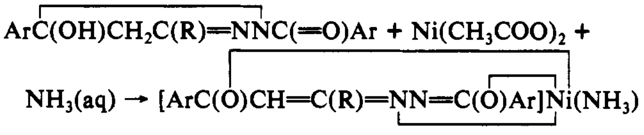
Results and Discussion

Benzoic acid–2-(1-alkyl/aryl-3-oxo-3-aryl-1-propenyl) hydrazide derivatives are formed by the condensation of benzoic acid hydrazide and 1,3-diketones.



$$ArCOCH_2COR + H_2NNHCOAr \rightarrow ArC(OH)CH_2C(R){=}NNC({=}O)Ar$$

These compounds behave as dibasic tridentate ligands and react with ammoniacal nickel acetate to form complexes of the following type:



$$ArC(OH)CH_2C(R){=}NNC({=}O)Ar + Ni(CH_3COO)_2 + NH_3(aq) \rightarrow [ArC(O)CH{=}C(R){=}NN{=}C(O)Ar]Ni(NH_3)$$

The ligands are white solids, are soluble in polar organic solvents, and are thermally unstable. The nickel complexes are brown in color, are soluble in common organic solvents, and decompose on heating.

The IR spectra of the ligands are consistent with the formation of benzoylhydrazones but are not useful for distinguishing the possible tautomers. The IR spectral bands observed for the ligands (Table IV) have been assigned considering that they exist exclusively in the cyclic tautomeric form as evident from ^{1}H NMR and X-ray studies. The O–H stretching vibration appears as a broad band in the region around 3300 cm^{-1}; two strong bands around 1680 and 1630 cm^{-1} are assigned to an amido carbonyl ν(C=O) and azomethine ν(C=N) stretching mode overlapping with other possible bands. The $-CH_2-$ bending vibration is observed at 1450 cm^{-1}, and O–H bending and C–O stretching modes are found around 1150 and 1320 cm^{-1}, respectively.[20]

The high-field ^{1}H NMR spectra of the compounds in $CDCl_3$, with TMS as internal standard (Table V) give evidence that they exist exclusively in the cyclic tautomeric form. No resonance signal corresponding to a methine proton, =CH–, is observed. The methylene, $-CH_2-$, signal appears around δ 2.9–4 ppm as a double doublet due to geminal coupling, $J_{HH'} = 19$ Hz, and the O–H proton appears as a broad peak in the region δ 5.4 ppm. The alkyl protons are observed around δ 1.09–2.35 ppm as singlets (R = CH_3) or multiplets (R = C_2H_5). The aromatic proton signal is observed as a multiplet in the region δ 7–8.08 ppm.

In the mass spectra of the ligands, the molecular ion peaks are observed for all species and other peaks corresponding to $M - OH^+$, $M - H_2O^+$, $ArCO^+$, Ar, and R, with a relatively higher intensity of RCO, are also observed.

In the IR spectra of the nickel complexes[21] (Table VI), N–H stretching of coordinated NH_3 is observed around 3200 cm^{-1}. The absence of absorption bands in the region 1725–1610 cm^{-1} excludes the possibility of a free or coordinated keto group in the chelated ligand. A strong band for the azomethine stretching mode, ν(C=N), is observed around 1600 cm^{-1}. This lowering is expected on coordination of nitrogen and electron delocalization in the chelate ring. The C–O bending mode appears as a strong band around 1160 cm^{-1}. The IR spectra of the complexes are in accordance with the tridentate bibasic behavior of the ligands.

The ^{1}H NMR spectra of the complexes in $CDCl_3$ with TMS as the internal standard (Table VII) give further evidence supporting the tridentate bibasic nature of the coordinated aryolhydrazones. The resonance signals corresponding to methylene

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Table II. Analytical and Mass Spectral Data and Melting Points of Aryolhydrazones

sample no.	Ar	R	Ar′	mp, °C	found, % (calc, %)			MS Data, M$^+$
					C	H	N	
1	4-FPh	CH_3	Ph	160	68.39 ((68.48)	4.95 (5.03)	9.30 (9.39)	298
2	4-FPh	CH_3	4-FPh	210	64.50 (64.58)	4.36 (4.42)	8.81 (8.85)	316
3	4-FPh	C_2H_5	Ph	230	69.19 (69.25)	5.40 (5.44)	8.90 (8.97)	312
4	4-FPh	C_2H_5	4-FPh	185	65.39 (65.48)	4.77 (4.84)	8.45 (8.48)	330
5	4-F-3-MePh	CH_3	Ph	240	69.18 (69.25)	5.40 (5.44)	8.91 (8.97)	312
6	4-F-3-MePh	CH_3	4-FPh	178	65.40 (65.48)	4.80 (4.84)	8.43 (8.48)	330
7	4-FPh	4-FPh	Ph	194	69.79 (69.86)	4.15 (4.23)	7.36 (7.40)	378
8	4-FPh	4-FPh	4-FPh	238	66.60 (66.69)	3.71 (3.78)	7.00 (7.06)	396

Table III. Analytical Data and Melting Points of Nickel Aryolhydrazone Complexes

sample no.	Ar	R	Ar′	mp, °C	found, % (calc, %)			
					C	H	N	Ni
1	4-FPh	CH_3	Ph	290	54.82 (54.90)	4.23 (4.30)	11.18 (11.29)	15.71 (15.78)
2	4-FPh	CH_3	4-FPh	260	52.30 (52.37)	3.77 (3.84)	10.71 (10.77)	15.00 (15.06)
3	4-FPh	C_2H_5	Ph	237	55.97 (56.02)	4.58 (4.66)	10.83 (10.88)	15.16 (15.21)
4	4-FPh	C_2H_5	4-FPh	255	53.44 (53.52)	4.15 (4.20)	10.32 (10.39)	14.50 (14.53)
5	4-F-3-MePh	CH_3	Ph	200	55.93 (56.02)	4.60 (4.66)	10.85 (10.88)	15.13 (15.21)
6	4-F-3-MePh	CH_3	4-FPh	210	53.45 (53.52)	4.15 (4.20)	10.33 (10.39)	14.49 (14.53)
7	4-FPh	4-FPh	Ph	280	58.38 (58.46)	3.70 (3.76)	9.19 (9.29)	12.81 (12.99)
8	4-FPh	4-FPh	4-FPh	260	56.19 (56.23)	3.32 (3.40)	8.83 (8.93)	12.36 (12.49)

Table IV. IR Spectral Data for Benzoylhydrazones (Values in cm^{-1}; KBr)[a]

sample no.	Ar	R	Ar′	O–H str	C=O str	C=N str	CH_2 bending (C=C str)	O–H bending	C–O str
1	4-FPh	CH_3	Ph	3300 br d	1680 s	1630 s	1450 s	1150 s	1320 s
2	4-FPh	CH_3	4-FPh	3300 br d	1680 s	1630 s	1450 s	1150 s	1320 s
3	4-FPh	C_2H_5	Ph	3290 br d	1680 s	1630 s	1445 s	1150 s	1325 s
4	4-FPh	C_2H_5	3-FPh	3290 br d	1675 s	1630 s	1450 s	1150 s	1325 s
5	4-F-3-MePh	CH_3	Ph	3300 br d	1680 s	1630 s	1445 s	1150 s	1320 s
6	4-F-3-MePh	CH_3	4-FPh	3300 br d	1680 s	1635 s	1445 s	1150 s	1320 s
7	4-FPh	4-FPh	Ph	3295 br d	1675 s	1635 s	1450 s	1145 s	1325 s
8	4-FPh	4-FPh	4-FPh	3300 br d	1680 s	1630 s	1445 s	1150 s	1320 s

[a] Abbreviations: str = stretching; br = broad; d = diffused; s = strong; m = medium.

Table V. ^1H NMR Spectral Data for Benzoylhydrazones ($CDCl_3$; TMS Internal Standard; Values in δ ppm)[a]

sample no.	Ar	R	Ar′	alkyl protons			ring methylene protons	O–H	arom protons
				ring substituted (R)		arom substituted			
				CH_3	CH_2	CH_3			
1	4-FPh	CH_3	Ph	2.07 br d			2.96 d 3.30 d	5.46 br s	7–7.96 m
2	4-FPh	CH_3	4-FPh	2.07 br d			2.95 d 3.31 d	5.45 br s	7–7.97 m
3	4-FPh	C_2H_5	Ph	1.09 t	2.34 q		2.95 d 3.30 d	5.45 br s	7–7.96 m
4	4-FPh	C_2H_5	4-FPh	1.09 t	2.34 q		2.96 d 3.29 d	5.46 br s	7–7.96 m
5	4-F-3-MePh	CH_3	Ph	2.06 br s		2.35 br s	2.97 d 3.29 d	5.47 br s	7–7.95 m
6	4-F-3-MePh	CH_3	4-FPh	2.06 br s		2.35 br s	2.97 d 3.29 d	5.46 br s	7–7.95 m
7	4-FPh	4-FPh	Ph				3.37 d 3.73 d	5.48 br s	7.04–8.08 m
8	4-FPh	4-FPh	4-FPh				3.36 d 3.73 d	5.48 br s	7.04–8.09 m

[a] Abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad.

Table VI. IR Spectral Data for Nickel Benzoylhydrazone Complexes (Values in cm^{-1}; KBr)

sample no.	Ar	R	Ar′	N–H str + C–H str	C=N str	C–O str
1	4-FPh	CH_3	Ph	3200 br d 3000 br d	1600 s	1160 s
2	4-FPh	CH_3	4-FPh	3200 br d	1600 s	1160 s
3	4-FPh	C_2H_5	Ph	3200 br d	1600 s	1160 s
4	4-FPh	C_2H_5	4-FPh	3200 br d	1600 s	1160 s
5	4-F-3-MePh	CH_3	Ph	3200 br d	1600 s	1160 s
6	4-F-3-MePh	CH_3	4-FPh	3200 br d	1600 s	1160 s
7	4-FPh	4-FPh	Ph	3200 br d	1600 s	1155 s
8	4-FPh	4-FPh	4-FPh	3200 br d		1155 s

Table VII. ^{1}H NMR Spectral Data for Nickel Benzoylhydrazone Complexes (($(CD_3)_2CO$; TMS Internal Standard; Values in δ ppm)

sample no.	Ar	R	Ar′	alkyl protons CH_3	CH_2	arom CH_3	=CH–	arom protons	NH_3 protons
1	4-FPh	CH_3	Ph	2.0 br s			5.86 s	7.0–8.0 m	2.35
2	4-FPh	CH_3	4-FPh	2.08 br s			5.86 s	7.0–8.0 m	2.35
3	4-FPh	C_2H_5	Ph	1.09 t	2.35 q		5.84 s	7.0–8.2 m	2.35
4	4-FPh	C_2H_5	4-FPh	1.09 t	2.35 q		5.84 s	7.0–8.2 m	2.35
5	4-F-3-MePh	CH_3	Ph	2.06 br s		2.35 br s	5.85 s	7.0–8.2 m	2.35
6	4-F-3-MePh	CH_3	4-FPh	2.06 br s		2.35 br s	5.86 s	7.0–8.2 m	2.35
7	4-FPh	4-FPh	Ph				5.83 s	7.0–8.2 m	2.40
8	4-FPh	4-FPh	4-FPh				5.83 s	7.0–8.2 m	2.40

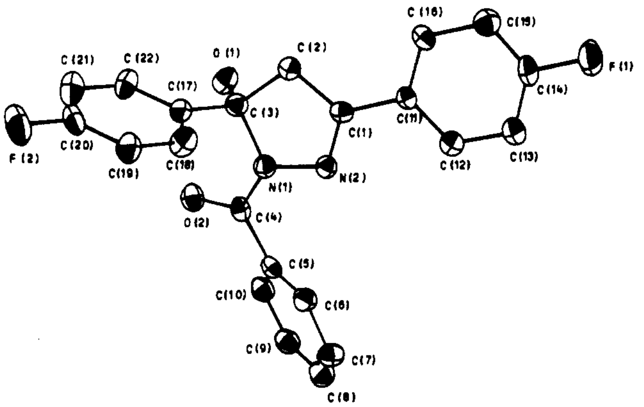

Figure 1. ORTEP plot of $C_{22}H_{16}F_2N_2O_2$ (I), showing 50% probability ellipsoids and the atom-labeling scheme.

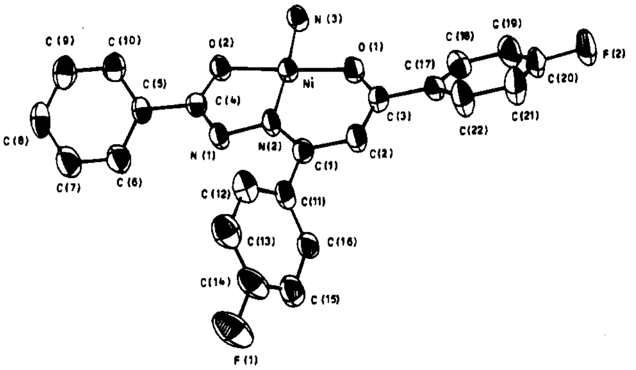

Figure 2. ORTEP plot of $C_{22}H_{17}F_2N_3O_2Ni$ (II), showing 50% probability ellipsoids and the atom-labeling scheme.

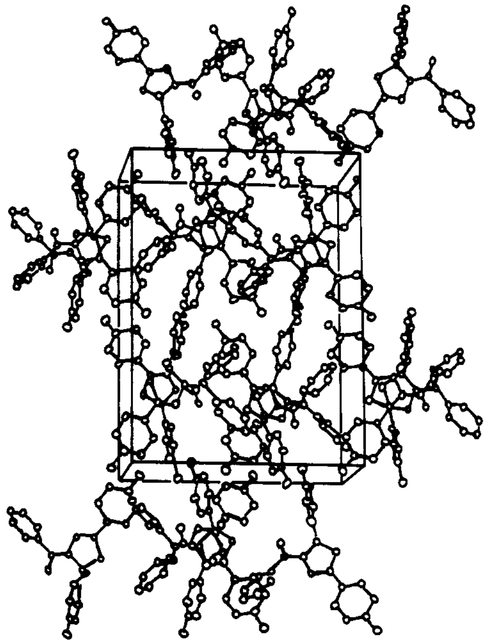

Figure 3. Unit cell packing of $C_{22}H_{16}F_2N_2O_2$ (I).

protons and hydroxy protons are not observed, and the signal observed in the region δ 5.8–6 ppm has been assigned to a methine proton; other signals for the alkyl and aryl have been assigned. The δ 2.4 ppm signal has been assigned to the protons of the coordinated NH_3 group and its position confirmed by deuterium exchange studies.

Molecular Structure of $C_6H_5C(=O)NN=C(p\text{-}FC_6H_4)\text{-}CH_2C(OH)(p\text{-}FC_6H_4)$ (I) and $[C_6H_5C(O)=NN=C(p\text{-}FC_6H_4)CH=C(O)(p\text{-}FC_6H_4)]Ni(NH_3)$ (II). The ORTEP plots of I and II are shown in Figures 1 and 2, and their unit cell molecular packing diagrams, in Figures 3 and 4, respectively. Positional parameters of the non-H atoms and the equivalent values of the anisotropic temperature factors for I and II are given in Tables VIII and IX, while bond lengths and angles are summarized in Tables X and XI, respectively.

The cyclic structure observed for the free ligand by ^{1}H NMR spectroscopy is also evident in the solid state by the crystal structure of compound I. The crystal data reveal that I exists as a five-membered diazo ring corresponding to a pyrazoline derivative (Figure 1). The least-squares plane program suggests that the heterocyclic ring is almost planar. The bond lengths N(1)–C(3) = 1.492 (6) Å and N(2)–C(1) Å = 1.285 (7) Å are of the order of a single and double bond, whereas the bond lengths

Table VIII. Positional Parameters and Their Estimated Standard Deviations for $C_{22}H_{16}F_2N_2O_2$ (I)

atom	*x*	*y*	*z*	*B*,[a] Å^2
F(1)	–0.2015 (4)	0.5768 (2)	0.5051 (2)	6.28 (9)
F(2)	–0.1670 (4)	0.2621 (2)	–0.0092 (2)	6.83 (9)
O(1)	0.2161 (3)	0.3614 (2)	0.2059 (2)	4.38 (8)
O(2)	0.1942 (3)	0.1929 (2)	0.2116 (2)	4.42 (9)
N(1)	0.0668 (4)	0.2805 (2)	0.2614 (2)	3.14 (9)
N(2)	0.0233 (4)	0.3123 (2)	0.3187 (2)	3.07 (8)
C(1)	0.0008 (5)	0.3898 (3)	0.3109 (2)	3.0 (1)
C(2)	0.0232 (5)	0.4218 (3)	0.2461 (3)	3.8 (1)
C(3)	0.0843 (5)	0.3460 (3)	0.2132 (2)	3.2 (1)
C(4)	0.1269 (4)	0.2066 (3)	0.2578 (2)	3.1 (1)
C(5)	0.1116 (5)	0.1444 (3)	0.3084 (2)	3.1 (1)
C(6)	–0.0019 (5)	0.1328 (3)	0.3402 (3)	4.0 (1)
C(7)	–0.0102 (6)	0.0712 (4)	0.3858 (3)	4.7 (1)
C(8)	0.0953 (6)	0.0225 (3)	0.4002 (3)	4.6 (1)
C(9)	0.2084 (6)	0.0336 (3)	0.3668 (3)	4.7 (1)
C(10)	0.2160 (5)	0.0945 (3)	0.3208 (3)	4.1 (1)
C(11)	–0.0488 (5)	0.4405 (3)	0.3629 (2)	2.9 (1)
C(12)	–0.0730 (5)	0.4033 (3)	0.4201 (2)	3.5 (1)
C(13)	–0.1266 (5)	0.4492 (3)	0.4691 (3)	4.1 (1)
C(14)	–0.1504 (5)	0.5315 (3)	0.4572 (3)	4.0 (1)
C(15)	–0.1275 (6)	0.5705 (3)	0.4025 (3)	4.3 (1)
C(16)	–0.0765 (5)	0.5235 (3)	0.3530 (3)	3.7 (1)
C(17)	0.0192 (5)	0.3223 (3)	0.1527 (2)	3.2 (1)
C(18)	–0.1099 (5)	0.2996 (4)	0.1536 (3)	4.4 (1)
C(19)	–0.1735 (6)	0.2779 (4)	0.0987 (3)	5.1 (1)
C(20)	–0.1050 (6)	0.2821 (3)	0.0450 (3)	4.5 (1)
C(21)	0.0208 (6)	0.3046 (4)	0.0413 (3)	5.1 (1)
C(22)	0.0840 (6)	0.3258 (4)	0.0968 (3)	4.5 (1)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

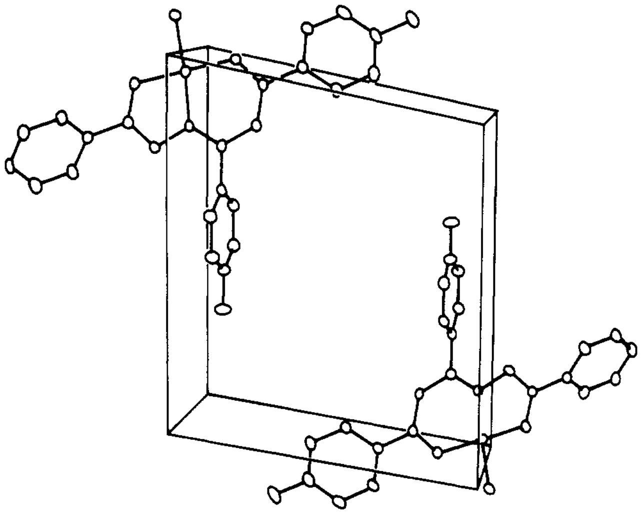

Figure 4. Unit cell packing of $C_{22}H_{17}F_2N_3O_2Ni$ (II).

Table IX. Positional Parameters and Their Estimated Standard Deviations for $C_{22}H_{17}F_2N_3O_2Ni$ (II)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ni	0.24972 (4)	0.02467 (3)	0.04626 (2)	2.915 (6)
F(1)	0.2763 (3)	0.1424 (2)	0.6664 (1)	6.63 (5)
F(2)	0.2783 (3)	0.7409 (2)	−0.2274 (2)	6.18 (5)
O(1)	0.2822 (2)	0.1793 (1)	−0.0152 (1)	3.37 (4)
O(2)	0.2090 (2)	−0.1292 (1)	0.1045 (1)	3.40 (4)
N(1)	0.2373 (3)	−0.0695 (2)	0.2648 (2)	3.30 (4)
N(2)	0.2521 (3)	0.0385 (2)	0.1882 (2)	3.06 (4)
N(3)	0.2506 (3)	−0.0082 (2)	−0.0978 (2)	3.92 (5)
C(1)	0.2709 (3)	0.1364 (2)	0.2241 (2)	3.03 (5)
C(2)	0.2919 (4)	0.2459 (2)	0.1504 (2)	3.42 (5)
C(3)	0.2915 (3)	0.2649 (2)	0.0386 (2)	3.12 (5)
C(4)	0.2155 (3)	−0.1520 (2)	0.2113 (2)	3.12 (5)
C(5)	0.1940 (3)	−0.2748 (2)	0.2726 (2)	3.16 (5)
C(6)	0.2730 (4)	−0.3331 (2)	0.3769 (2)	4.33 (6)
C(7)	0.2510 (4)	−0.4481 (3)	0.4333 (2)	4.95 (7)
C(8)	0.1481 (4)	−0.5049 (2)	0.3874 (2)	4.51 (7)
C(9)	0.0695 (4)	−0.4483 (2)	0.2845 (2)	4.41 (7)
C(10)	0.0925 (4)	−0.3342 (2)	0.2270 (2)	3.82 (6)
C(11)	0.2701 (3)	0.1367 (2)	0.3423 (2)	3.10 (5)
C(12)	0.1212 (4)	0.1222 (2)	0.4070 (2)	3.82 (6)
C(13)	0.1226 (4)	0.1255 (3)	0.5159 (2)	4.53 (7)
C(14)	0.2718 (4)	0.1436 (2)	0.5585 (2)	4.27 (7)
C(15)	0.4203 (4)	0.1585 (2)	0.4980 (2)	4.17 (6)
C(16)	0.4177 (4)	0.1561 (2)	0.3890 (2)	3.51 (6)
C(17)	0.2970 (3)	0.3900 (2)	−0.0314 (2)	3.22 (5)
C(18)	0.3617 (4)	0.3956 (3)	−0.1355 (2)	4.11 (6)
C(19)	0.3595 (4)	0.5137 (3)	−0.2017 (2)	4.87 (7)
C(20)	0.2883 (4)	0.6241 (2)	−0.1615 (2)	4.18 (6)
C(21)	0.2249 (5)	0.6232 (3)	−0.0597 (3)	5.37 (8)
C(22)	0.2304 (5)	0.5051 (3)	0.0060 (2)	5.05 (7)
H(2)	0.303 (3)	0.313 (2)	0.182 (2)	1.8 (5)*
H(3a)	0.262 (4)	0.045 (3)	−0.141 (3)	4.7 (8)*
H(3b)	0.343 (5)	−0.067 (4)	−0.104 (3)	7 (1)*
H(3c)	0.160 (5)	−0.016 (3)	−0.111 (3)	6 (1)*
H(6)	0.346 (3)	−0.299 (2)	0.408 (2)	1.7 (5)*
H(7)	0.320 (4)	−0.493 (2)	0.506 (2)	3.7 (7)*
H(8)	0.133 (4)	−0.576 (3)	0.419 (2)	3.4 (7)*
H(9)	−0.010 (4)	−0.482 (2)	0.251 (2)	2.6 (6)*
H(10)	0.033 (3)	−0.295 (2)	0.157 (2)	1.9 (5)*
H(12)	0.024 (3)	0.112 (2)	0.375 (2)	1.5 (5)*
H(13)	0.026 (4)	0.118 (2)	0.557 (2)	2.8 (6)*
H(15)	0.525 (3)	0.163 (2)	0.533 (2)	1.4 (4)*
H(16)	0.523 (3)	0.163 (2)	0.345 (2)	2.5 (6)*
H(18)	0.407 (3)	0.319 (2)	−0.162 (2)	2.0 (5)*
H(19)	0.404 (4)	0.515 (3)	−0.273 (2)	3.3 (7)*
H(21)	0.174 (5)	0.702 (3)	−0.034 (3)	5.4 (9)*
H(22)	0.174 (4)	0.507 (3)	0.074 (2)	3.4 (7)*

[a] Starred *B* values are for atoms that were refined isotropically. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table X. Intramolecular Distances (Å) and Angles (deg) for $C_{22}H_{16}F_2N_2O_2$ (I)[a]

(a) Bonds			
O(1)–C(3)	1.412 (7)	N(1)–C(4)	1.351 (7)
O(2)–C(4)	1.237 (6)	N(2)–C(1)	1.286 (6)
N(1)–N(2)	1.408 (6)	C(1)–C(2)	1.501 (7)
N(1)–C(3)	1.492 (6)	C(2)–C(3)	1.551 (8)
(b) Angles			
N(2)–N(1)–C(3)	112.7 (3)	C(1)–C(2)–C(3)	102.4 (4)
N(2)–N(1)–C(4)	121.7 (4)	O(1)–C(3)–N(1)	108.8 (4)
C(3)–N(1)–C(4)	122.0 (4)	O(1)–C(3)–C(2)	108.4 (5)
N(1)–N(2)–C(1)	107.6 (4)	N(1)–C(3)–C(2)	101.2 (4)
N(2)–C(1)–C(2)	115.3 (4)	O(2)–C(4)–N(1)	118.0 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table XI. Intramolecular Distances (Å) and Angles (deg) for $C_{22}H_{17}F_2N_3O_2Ni$ (II)[a]

(a) Bonds			
Ni–O(1)	1.822 (2)	N(1)–N(2)	1.402 (3)
Ni–O(2)	1.835 (2)	N(1)–C(4)	1.308 (4)
Ni–N(2)	1.827 (3)	N(2)–C(1)	1.322 (4)
Ni–N(3)	1.927 (2)	C(1)–C(2)	1.413 (3)
O(1)–C(3)	1.309 (3)	C(2)–C(3)	1.376 (3)
O(2)–C(4)	1.312 (3)		
(b) Angles			
O(1)–Ni–O(2)	177.75 (8)	N(2)–N(1)–C(4)	107.8 (2)
O(1)–Ni–N(2)	97.19 (8)	Ni–N(2)–N(1)	114.7 (2)
O(1)–Ni–N(3)	88.40 (9)	Ni–N(2)–C(1)	126.9 (2)
O(2)–Ni–N(2)	84.21 (8)	N(1)–N(2)–C(1)	118.4 (2)
O(2)–Ni–N(3)	90.25 (9)	N(2)–C(1)–C(2)	120.6 (2)
N(2)–Ni–N(3)	174.23 (9)	C(1)–C(2)–C(3)	126.0 (3)
Ni–O(1)–C(3)	125.0 (1)	O(1)–C(3)–C(2)	124.3 (2)
Ni–O(2)–C(4)	110.4 (2)	O(2)–C(4)–N(1)	122.7 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

of the atoms attached to C(2) and C(3) including the C(2)–C(3) bond length are of the order of a single bond.[22-24] The C(3) atom represents an asymmetric center, and therefore, optical isomers for these compounds are possible. However, in the unresolved mixture their existence could not be detected by ^{1}H NMR studies.

The X-ray data for complex II show that the donor atoms impose a square-planar geometry around the nickel atom (Figure 2). The ligands bind the metal tridentately forming O_2N donor systems, and an NH_3 molecule is also coordinated to the central metal atom. The bond lengths and angles (Table XI) give evidence for the bifunctional tridentate behavior of the ligand. The bond lengths C(4)–O(2) = 1.312 (3) Å, C(3)–O(1) = 1.309 (3) Å, and N(1)–N(2) = 1.402 (3) Å approximate single-bond lengths whereas C(4)–N(1) = 1.308 (4) Å and C(1)–N(2) = 1.322 (4) Å are of the order of a double bond.[24,25] These observations give additional evidence that the coordinated form of the ligand corresponds to the enol tautomeric form (B).

The chelate rings of the ligand are essentially in the same plane as the central metal, and the phenyl rings are however nonplanar. The observed variations in the lengths from the standard values are attributed to electron delocalization in the chelate ring.

Conclusion

From the studies, it can be concluded that the aryolhydrazones of 1,3-diketones exist predominantly in a cyclic tautomeric from both in solution as well as in solid state. These ligands undergo a ring-opening reaction on complexation with nickel, behaving as bifunctional tridentate ligands corresponding to the enol tau-

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tomer of the hydrazone form (B).

Acknowledgment. K.C.J. is thankful to the CSIR, New Delhi, for financial assistance. We thank the UGC, New Delhi, for providing the X-ray diffractometer facilities.

Supplementary Material Available: Tables SI–SVII, listing bond lengths, bond angles, thermal parameters, and crystallographic data for $C_{22}H_{16}F_2N_2O_2$ (I) and $C_{22}H_{17}F_2N_3O_2Ni$ (II) (13 pages); tables of observed and calculated structure factors for I and II, respectively (43 pages). Ordering information is given on any current masthead page.

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Metal Ion Complexes of Water-Soluble Calix[4]arenes

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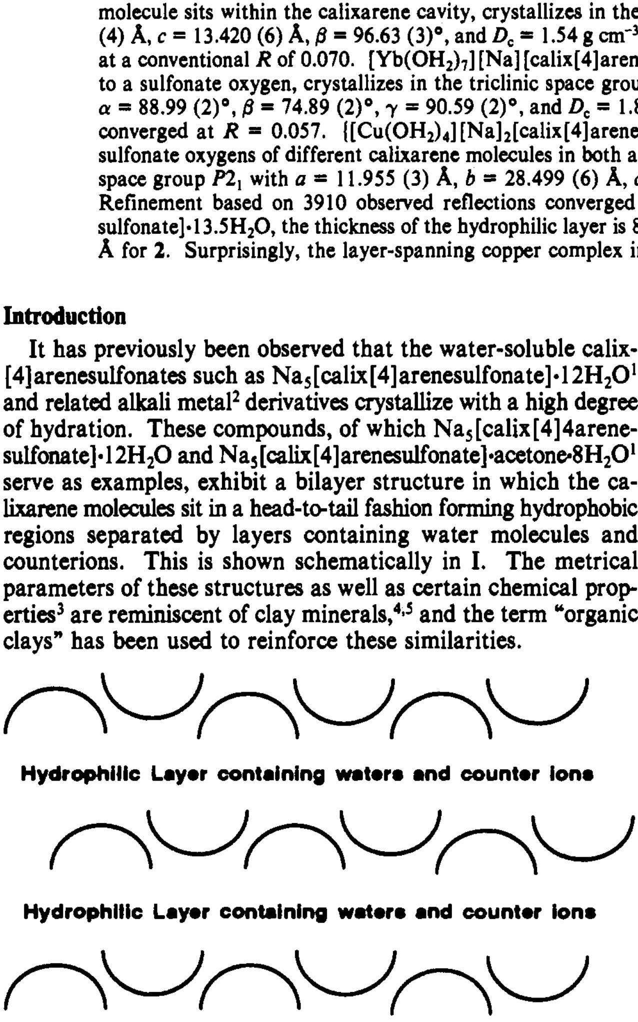
Received December 4, 1990

Three transition metal complexes of water-soluble calixarenes have been prepared and structurally characterized, demonstrating the three possible modes of incorporation of metals into the solid-state layered structure. $[Cr(OH_2)_6][Na][calix[4]arenesulfonate](acetone)\cdot 10.5H_2O$ (**1**), in which the $Cr(OH_2)_6^{3+}$ species is intercalated within the hydrophilic layer and an acetone molecule sits within the calixarene cavity, crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.206$ (6) Å, $b = 31.251$ (4) Å, $c = 13.420$ (6) Å, $\beta = 96.63$ (3)°, and $D_c = 1.54$ g cm^{-3} for $Z = 4$. Refinement based on 3518 observed reflections converged at a conventional R of 0.070. $[Yb(OH_2)_7][Na][calix[4]arenesulfonate]\cdot 9H_2O$ (**2**), in which a $Yb(OH_2)_7^{3+}$ moiety binds directly to a sulfonate oxygen, crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.362$ (3) Å, $b = 13.656$ (3) Å, $c = 13.964$ (3) Å, $\alpha = 88.99$ (2)°, $\beta = 74.89$ (2)°, $\gamma = 90.59$ (2)°, and $D_c = 1.80$ g cm^{-3} for $Z = 2$. Refinement based on 4210 observed reflections converged at $R = 0.057$. $\{[Cu(OH_2)_4][Na]_2[calix[4]arenesulfonate]\cdot 7.5H_2O\}_2$ (**3**), in which $Cu(OH_2)_4^{2+}$ units interact with sulfonate oxygens of different calixarene molecules in both an intralayer and an interlayer fashion, crystallizes in the monoclinic space group $P2_1$ with $a = 11.955$ (3) Å, $b = 28.499$ (6) Å, $c = 12.442$ (3) Å, $\beta = 91.49$ (2)°, and $D_c = 1.66$ g cm^{-3} for $Z = 4$. Refinement based on 3910 observed reflections converged at a conventional R of 0.054. In the parent $Na_4[calix[4]arenesulfonate]\cdot 13.5H_2O$, the thickness of the hydrophilic layer is 8.41 Å. The corresponding thickness in **1** is 9.98 Å compared to 7.51 Å for **2**. Surprisingly, the layer-spanning copper complex in **3** reduces this distance only slightly to 8.02 Å.

Introduction

It has previously been observed that the water-soluble calix[4]arenesulfonates such as $Na_5[calix[4]arenesulfonate]\cdot 12H_2O$[1] and related alkali metal[2] derivatives crystallize with a high degree of hydration. These compounds, of which $Na_5[calix[4]4arenesulfonate]\cdot 12H_2O$ and $Na_5[calix[4]arenesulfonate]\cdot acetone\cdot 8H_2O$[1] serve as examples, exhibit a bilayer structure in which the calixarene molecules sit in a head-to-tail fashion forming hydrophobic regions separated by layers containing water molecules and counterions. This is shown schematically in I. The metrical parameters of these structures as well as certain chemical properties[3] are reminiscent of clay minerals,[4,5] and the term "organic clays" has been used to reinforce these similarities.



I

There have been several reports of the interaction of metal ions with calixarenes.[6-15] These have invariably been based on either complexation of the metal by the phenolic oxygen atom or reaction of metal complexes with the phenolic protons of *p-tert*-butylcalixarene. Introduction of a group capable of binding metals such as sulfonate in the position para to the phenolic group opens new possible metal ion coordination modes, and the involvement of these groups with the water molecules of the hydrophilic layer presents an interesting opportunity to study the coordination chemistry of the sulfonate groups with hydrated metal ions.

One can envision three possible modes of interaction between the calix[4]arenesulfonate and a transition metal ion within a layered structure: (1) intercalation of the metal-containing species into the inter-calix layer with no direct metal-sulfonate oxygen bond; (2) interaction between the metal ion and the sulfonate groups of one calixarene unit; (3) interaction between the metal ion and the sulfonate groups of more than one calixarene. The three complexes reported here serve as examples of each of these possibilities.

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