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Crystalline Compounds of Urea and Thiourea with Acetylacetonato Complexes[2]

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In the course of a search for possible resolution procedures for neutral tris(acetylacetonato) complexes, we have observed the formation of crystalline compounds by the reaction of neutral tris(acetylacetonato) complexes with urea or thiourea. The compounds have the general formulas $M(acac)_3 \cdot 3urea$ and $M(acac)_3 \cdot 2thiourea$. The properties of the crystals, and their behavior on being dissolved, indicate that neither urea nor thiourea is bound in the first coordination sphere of the metal ion.

Under similar conditions, bis(acetylacetonato)cobalt(II) forms the compounds $Co(acac)_2 \cdot 2urea$ and $Co(acac)_2 \cdot 2thiourea$. In these cases the urea or thiourea is probably bound in the first coordination sphere of the metal ion.

Experimental Section

The tris(acetylacetonato) complexes of the following tervalent metal ions were made by literature methods: Al(III),[3] Co(III),[4] Cr(III),[5] Fe(III),[6] Mn(III),[7] and Rh(III).[8] The new compounds reported in this work are made simply by addition of a saturated solution of urea or thiourea in methanol to a saturated solution of the tris(acetylacetonato) complex in methanol. In the case of the thiourea compounds the precipitation is instantaneous, whereas the urea compounds require anywhere from 10 to 30 min before crystals appear.

The colors of the compounds are similar to those of the original complex acetylacetonate. The most notable difference between these compounds and the parent complex is in solubility characteristics. The acetylacetonate solid is soluble in solvents such as benzene, carbon tetrachloride, and other organic solvents; the addition compounds with urea and thiourea are not soluble in these solvents. The urea and thiourea adducts of the complex acetylacetonates are partially soluble in water and in time are completely destroyed in water, and the complex acetylacetonate can be isolated without change.

Since the solids form only in a high concentration of urea or thiourea, purification of the solid by recrystallization is not possible. Although the solids are quite soluble in methanol, they can be washed with cold methanol to remove solution adhering to the crystals, without excessive loss. During the production and growth of crystals of colored complexes no colorless crystals of urea or thiourea were observed; nor were colorless crystals observed when such isolated solids were examined under a microscope. On the basis of these facts the solids are considered to be crystalline phases of distinct composition.

TABLE I
ANALYTICAL DATA

Compound	% calculated					% found				
	C	H	N	S	M	C	H	N	S	M
$M(acac)_3 \cdot 3$ urea										
M = Al	42.86	6.59	16.66	...	5.35	42.51	6.70	16.58	...	5.14
M = Co	40.30	6.20	15.67	...	10.99	39.74	6.38	14.88	...	10.59
						40.21	6.43	15.61	...	10.98
M = Cr	40.83	6.28	15.87	...	9.82	40.70	6.70	14.65	...	9.35
						40.18	6.56	15.38	...	9.40
M = Fe	40.54	6.24	15.76	...	10.47	39.18	6.52	15.27	...	10.19
						40.15	6.70	15.49	...	10.60
M = Rh	37.25	5.73	14.48	...	17.73	37.21	6.21	14.42	...	16.10
						36.88	5.71	14.56	...	17.25
$M(acac)_3 \cdot 2$ thiourea										
M = Al	42.85	6.13	11.76	13.46	5.66	42.60	6.09	11.38	11.70	5.50
						42.19	6.25	12.04	11.49	4.51
M = Co	40.15	5.75	11.02	12.61	11.59	39.90	5.81	11.59	14.02	12.99
						39.28	5.65	11.56	13.00	11.72
M = Cr	40.71	5.83	11.17	12.79	10.37	40.89	5.99	11.23	12.42	10.83
						40.32	5.88	11.21	12.50	10.28
M = Fe	40.40	5.78	11.09	12.69	11.05	40.18	5.81	11.03	12.79	11.09
						40.15	5.85	11.17	12.80	11.31
M = Mn	40.47	5.79	11.11	12.71	10.89	40.64	5.86	11.37	13.81	10.25
M = Rh	36.96	5.29	10.14	11.61	18.63	37.18	5.48	10.11	11.30	18.65
						37.06	5.25	10.23	11.82	19.08
$Co(acac)_2 \cdot 2X$										
X = urea	38.20	5.88	14.85	...	15.62	37.45	5.86	14.58	...	14.60
X = thiourea	35.21	5.42	13.69	15.66	14.40	34.96	5.38	13.86	14.83	15.63
						34.48	5.33	13.74	13.23	12.54

Anhydrous bis(acetylacetonato)cobalt (II) was prepared by a literature method.[9] The compounds with urea and thiourea were prepared in the same way as for the ternary complexes.

The analytical data for the crystalline solids formed are given in Table I. Where more than one analysis is given for a com-

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[2] Presented in part at the Southeast-Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 2–4, 1965.

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pound, the analyses were performed on samples prepared at different times.

Discussion

The evidence suggests that the compounds containing tris(acetylacetonato) complexes are similar to the halomethane solvates of these complexes reported by Steinbach and co-workers.[10] The most obvious feature of the infrared spectra of the solids is in the 3-μ region, in which N–H vibrations appear. The compounds containing thiourea show three characteristic peaks, with positions and intensities like those of thiourea itself.[11] Urea itself has two characteristic strong peaks[11,12] at about 3330 and 3440 cm^{-1}. In the M(acac)$_3$·3urea compounds an additional strong band appears at about 3170 cm^{-1}. The difficulties of assigning bands in this region have been discussed by Badger and Waldron,[12] but the presence of the additional band is strongly indicative of hydrogen bonding to the acetylacetonato complex. Thus hydrogen bonding appears to be important in the urea compounds, but not in the thiourea compounds.

The formulas and properties of the compounds containing cobalt(II) suggest that these have a structure like that of bis(acetylacetonato)cobalt(II) dihydrate.[13]

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Proton Magnetic Resonance Studies of Pyridine Complexes of Bis(benzoylacetonato)nickel(II) and -cobalt(II)

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Spin delocalization in pyridine complexed with nickel(II) and cobalt(II) acetylacetonates, M(AA)$_2$, has been reported by Happe and Ward.[1] Using proton magnetic resonance these workers concluded that the frequency changes observed for the pyridine protons in the presence of the nickel complex could be interpreted as contact shifts, ν_c, due principally to spin delocalization in a σ orbital of the pyridine ring. The shifts observed in the presence of Co(AA)$_2$ were interpreted as being due to contact shifts and dipolar (pseudo-contact) shifts, ν_ψ, operating in opposite directions. The present work involving nickel(II) and cobalt(II) benzoylacetonates, M[–OC(C$_6$H$_5$)CHC(CH$_3$)O–]$_2$, M(BA)$_2$, provides an additional and more extensive test of this interpretation.

Experimental Section

2:1 Complexes of Pyridine and M(BA)$_2$.—Anhydrous M(BA)$_2$ (M = Ni, Co) was prepared by a previously described method.[2] To solutions of the anhydrous chelate in toluene was added an excess of pyridine. Heptane was added, and the crystallized 2:1 complex was isolated by filtration and dried *in vacuo* for 8 hr. The green nickel complex melted at 163–165° with previous softening.[3] The orange cobalt complex melted at 147–148° with preliminary softening. The visible–near-infrared spectrum of the cobalt complex in chloroform 2.0 *M* in pyridine showed a peak at 9850 cm^{-1} and a shoulder at 18,300 cm^{-1}. In pure pyridine the low-frequency cobalt d–d transition shifted slightly to 9760 cm^{-1}. X-Ray powder diffraction patterns of the cobalt and nickel complexes were identical. *Anal.* Calcd for $C_{30}H_{28}N_2O_4Co$: C, 66.79; H, 5.23. Found: C, 67.00; H, 5.32.

Nuclear Magnetic Resonance Spectra.—These were obtained using a modified Varian A-60A spectrometer capable of scanning from below −4000 to above +4000 cps using tetramethylsilane as an internal standard with downfield being the negative direction. The peaks observed in a deuteriochloroform solution of Co(BA)$_2$ with an excess of pyridine were assigned on the basis of their intensities. The β-pyridine and *m*-phenyl proton resonances appear as doublets and the γ-pyridine and *p*-phenyl resonances as triplets whereas the α-pyridine and *o*-phenyl resonances are broadened singlets due to the rapid relaxation of these protons. In pure pyridine the observed isotropic shifts for the benzoylacetonate protons were: CH$_3$, −1165; CH, −945; *o*-C$_6$H$_5$, −1755; *m*-C$_6$H$_5$, −630; *p*-C$_6$H$_5$, −410 cps.

The nickel(II) complex showed much broader resonance peaks which were more difficult to resolve and assign. Assignment was made on the basis of relative intensities and broadening: α-pyridine > β-pyridine > γ-pyridine; CH > *o*-C$_6$H$_5$, CH$_3$ > *m*-, *p*-C$_6$H$_5$.

Results and Discussion

The isotropic shifts, $\Delta\nu_i$, attributable to the 2:1 pyridine:M(BA)$_2$ complexes in deuteriochloroform solutions at 39° are given in Table I. For the benzoylacetonate protons these values are the differences between the directly observable resonances and the diamagnetic positions. The isotropic shifts for the pyridine protons in the 2:1 complex were similarly

TABLE I

ISOTROPIC SHIFTS AND GEOMETRIC FACTORS FOR 2:1 PYRIDINE:M(BA)$_2$ COMPLEXES[a]

Proton	Diamagnetic chem shifts, cps	Isotropic shift, $\Delta\nu_i$ Ni(BA)$_2$	Co(BA)$_2$	Geometric factor[b] Calcd	Exptl
α-Pyridine	−515	−5990	−2915	+0.0201	+0.0205
β-Pyridine	−440	−1820	−145	+0.0113	+0.0113
γ-Pyridine	−455	−450	+1050	+0.0102	+0.0100
CH$_3$	−125	−195	−1320	−0.0082	−0.0075
CH	−370	+1120	−1295	−0.0117	−0.0154
o-C$_6$H$_5$	−465	−110	−1800	−0.0096	−0.0113
m-C$_6$H$_5$	−445	−155	−645	−0.0028	−0.0033
p-C$_6$H$_5$	−445	−5	−415	−0.0019	−0.0027

[a] Shift data in cps were obtained at 39° in deuteriochloroform solutions containing 0.084 mmole/ml of M(BA)$_2$ and 1.90 mmole/ml of pyridine. Similar results were obtained with half the concentration of M(BA)$_2$ or with preformed M(BA)$_2$·2C$_5$H$_5$N.
[b] $(3 \cos^2 \chi - 1)r^{-3}$ in A^{-3}.

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