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]

---

[10] J. F. Steinbach and J. H. Burns, *J. Am. Chem. Soc.*, **80**, 1839 (1958); F. R. Clarke, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **26**, 1311 (1964).

[11] J. E. Stewart, *J. Chem. Phys.*, **26**, 248 (1957).

[12] R. M. Badger and R. D. Waldron, *ibid.*, **26**, 255 (1957).

[13] G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

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

BY RUDOLPH W. KLUIBER AND WILLIAM DEW. HORROCKS, JR.

Received June 18, 1966

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}.

---

[1] J. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

[2] F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

[3] (a) R. Nast and H. Ruckemann, *Ber.*, **93**, 2329 (1960); (b) J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **87**, 2821 (1965).

obtained except that the observed time-averaged shifts were corrected for the presence of excess uncomplexed pyridine using the expression $\Delta\nu_i = \Delta\nu_o/N_p$ where $\Delta\nu_o$ is the observed shift and N_p is the mole fraction of complexed pyridine.[4] The values for the β and γ protons in complexed pyridine were independently obtained from spectra taken at −50°. At this temperature ligand exchange is slow and the pure paramagnetic resonance positions can be observed. The isotropic shifts thus obtained, after correcting to 39° using the Curie relationship, agreed with the values given in Table I to within ±10 cps. The ratios of the proton frequency shifts for pyridine complexed with $Ni(BA)_2$ $\alpha:\beta:\gamma = 10.0:3.04:0.75$ are almost identical with those reported by Happe and Ward.[1] These ratios are also similar to those reported for "tetrahedrally" coordinated nickel complexes of pyridine[5] although the total amount of spin delocalized appears to be less in the present system. The pyridine proton ratios in the $Co(BA)_2$ complex differ from those reported for the $Co(AA)_2$ complex although they are qualitatively similar. Unfortunately the exchange of pyridine in the $Co(BA)_2$ complex is still rapid at −50° and no independent check of the absolute isotropic shift of the pyridine protons is available.

Pseudo-contact shifts are assumed to follow eq 1,[6] where ν is the frequency of the spectrometer and χ

$$\Delta\nu_\psi = -\frac{\nu\beta^2 S(S+1)}{45kT}\left[\frac{3\cos^2\chi - 1}{r^3}\right](3g_{\parallel}^2 + g_{\parallel}g_{\perp} - 4g_{\perp}^2) \quad (1)$$

is the angle between $g_{\parallel}$, which here is presumed coincident with the principal molecular axis, and a vector of length r joining the central metal atom and the given proton. This equation is based on an axially symmetric model involving a system in which the electron spin relaxation time is short compared to the rotational correlation time. The 2:1 cobalt and nickel complexes are isostructural and, by analogy with the acetylacetonate system, probably involve coordination of the pyridines in the *trans* axial positions.[3b] The geometric factors, $(3\cos^2\chi - 1)r^{-3}$, for such a model are given in Table I. Those for the pyridine ring were taken from the previous work,[1] while those for the benzoylacetonate protons were calculated using a construction based on the structure of the copper chelate.[7] Simplifications used include the assumptions that the β-diketone ring is symmetrical and planar, that the Co–O bond distance is 2.0 A, and that the phenyl group occupies a preferred conformation, due to conjugation, which is coplanar with the β-diketone ring although rapidly rotating between equivalent conformers (*i.e.*, the two *ortho* positions are equivalent as are the two *meta* positions). The geometric factors thus calculated are compared with "experimentally" derived geometric factors. The "experimental" geometric factors were obtained by assuming that the contact shifts for the nickel and cobalt complexes are the same. The "experimental" pseudo-contact shifts, $\Delta\nu_i - \Delta\nu_c$, thus obtained were reduced by a factor of 1.5×10^5 to give the "experimental" geometric factors (Table I). The semiquantitative agreement of these two sets of geometric factors strongly supports the conclusion that pseudo-contact shifts are of significant importance in high-spin, tetragonally distorted, hexacoordinate cobalt(II) complexes.

The assumption made in calculating the "experimental" geometric factors, namely, that the contact shifts of the nickel and cobalt complexes are the same, appears justifiable in the present system since similar assumptions have led to reasonable conclusions in other studies involving nickel and cobalt acetylacetonates.[8] The particularly small contact shifts of the β-diketone phenyl ring protons also justifies this assumption as contact shifts even twice as large as in the cobalt complex would not change the semiquantitative agreement materially. Furthermore, using eq 1 (strictly valid only for systems having no residual ground-state orbital angular momentum[9]), a magnetic moment of 4.82 BM ($Co(AA)_2$ in pyridine[2]), and the formula $\mu = g[S(S+1)]^{1/2}$, values of $g_{\parallel} = 1.92$ and $g_{\perp} = 2.79$ were calculated. A value of $g_{\parallel} = 2.0$ is expected for a tetragonally distorted, octahedral cobalt(II) complex which has an A_{2g} ground state and in which the T_{1g} (F) energy level splitting due to distortion is large compared to kT or λ.[10]

Exact agreement between the "experimental" and calculated geometric factors probably cannot be expected. Eaton's[11] analysis of the tris(acetylacetonates) suggests that a greater proportion of spin should be delocalized in a π-antibonding rather than a π-bonding orbital of the benzoylacetonate for the cobalt compared with the nickel complex. Different contributions from σ and π delocalization can also add to the discrepancies. Furthermore, the assumption of D_{4h} symmetry in these complexes is at best approximate as the X-ray structural analyses of the copper and vanadyl complexes indicate a nonequivalence of the two keto groups.[7] The phenyl ring may also deviate from coplanarity with the chelate ring in solution as it does in the crystal owing to steric effects of the biphenyl type. The further assumption that spin is delocalized as effectively in the axial and equatorial directions in both the cobalt and nickel complexes is unwarranted and only permissible because the con-

---

(4) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

(5) R. H. Holm, G. W. Everett, Jr., and W. D. Horrocks, Jr., *ibid.*, **88**, 1071 (1966). Similar ratios have been reported for cobalt(II)–pyridine complexes in which the dipolar shifts are expected to be small: E. E. Zaev, G. I. Skubnevskaya, and Y. N. Molin, *J. Struct. Chem.* (USSR), **6**, 610 (1965); *Zh. Strukt. Khim.*, **6**, 639 (1965).

(6) D. R. Eaton and W. D. Phillips, "Advances in Magnetic Resonance," J. S. Waugh, Ed., Vol. 1, Academic Press Inc., New York, N. Y., 1965, p 103.

(7) P. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, **5**, 516 (1966).

(8) W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964); R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **87**, 5350 (1965); **88**, 1399 (1966).

(9) W. D. Horrocks, Jr., R. H. Fisher, J. R. Hutchison, and G. N. LaMar, *ibid.*, **88**, 2436 (1966); Z. Luz and R. G. Schulman, *J. Chem. Phys.*, **43**, 3750 (1965).

(10) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 85 (1964).

(11) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

tact shifts for the equatorially situated protons are generally small compared with the pseudo-contact shifts. Despite these sources of error, the simple analysis presented here demonstrates that the benzoylacetonate proton shifts in the cobalt complex are predominantly dipolar in nature.

Acknowledgment.—This research was supported by the National Science Foundation through Grant No. NSF GP3397.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MERRIMACK COLLEGE, NORTH ANDOVER, MASSACHUSETTS,
AND THE DEPARTMENT OF CHEMISTRY,
LOWELL TECHNOLOGICAL INSTITUTE, LOWELL, MASSACHUSETTS

sym-Diisocyanatotetraorganodisilanes[1]

BY RONALD M. PIKE[2] AND EDWARD B. MOYNAHAN

Received July 15, 1966

The synthesis and characterization of two representatives of a new class of organofunctional disilanes, the *sym*-diisocyanatotetraorganodisilanes, $OCN(R)_2SiSi(R)_2NCO$, wherein $R = CH_3$ or C_6H_5 is reported. Compounds containing the silicon isocyanate linkage (Si–NCO) have been known for some time and studies on the addition of amines to this isocyanate linkage have been reported.[3] Goubeau and Henbach[4] have shown that this addition reaction leads to the formation of silylureas. Furthermore, Neville and McGee[3] illustrated these ureas to be easily hydrolyzed by moisture to yield a substituted urea.

$$4RR'NH + Si(NCO)_4 \longrightarrow Si(NHCONRR')_4 \xrightarrow{2H_2O} 4H_2NCONRR' + SiO_2$$

These workers used this reaction as a means of preparing N-mono- and N,N-disubstituted ureas. To our knowledge, the only isocyanatodisilane previously reported was pentamethyldisilanyl isocyanate, $(CH_3)_3SiSi(CH_3)_2NCO$, prepared by Urenovitch and MacDiarmid.[5] The synthesis of the *sym*-diisocyanatotetraorganodisilanes reported in the present work offers an advantage of difunctionality. Thus, the incorporation of the disilane linkage into various polymeric systems through addition reactions to the isocyanate units should be possible.

The diisocyanatotetraorganodisilanes were prepared from the corresponding *sym*-dichlorotetraorganodisilane derivatives. The tetramethyl-[6] and tetraphenyldisilanes,[7] $Cl(R)_2SiSi(R)_2Cl$, where $R = CH_3$ or C_6H_5, were obtained through known routes. These disilanes were shown to be free of siloxane (Si–O–Si) impurities by infrared analysis. Treatment of these intermediates with silver isocyanate led to the formation of the desired compounds.

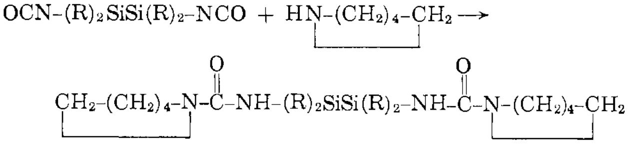
$$Cl(R)_2SiSi(R)_2Cl \xrightarrow{AgNCO} OCN(R)_2SiSi(R)_2NCO \qquad R = CH_3 \text{ or } C_6H_5$$

These new materials are very sensitive to moisture and oxygen. Consequently, all work was carried out under a deoxygenated, anhydrous nitrogen atmosphere.

It was of interest to determine (a) whether or not the $\equiv Si—N=$ linkage is as unstable in a *sym*-diuredotetraorganodisilane derivative as are the silylureas of Neville and McGee[3] and (b) whether or not a nucleophilic species could be added to the isocyanate function without cleavage of the disilane linkage.

The first problem was solved by an analytical technique used to determine the Si–Si linkage,[7] *i.e.*, the determination of the hydrogen value of the materials. A weighed amount of the compound was decomposed in moist piperidine and the resulting hydrogen gas collected and measured. Analysis of the reaction mixture for both the diisocyanatotetramethyl- and -tetraphenyldisilanes gave a solid product shown to be piperidine carboxamide. This result indicates that the Si–N linkage in these compounds is susceptible to hydrolytic cleavage.

Piperidine was selected as the initial nucleophilic species. Treatment of the two isocyanate derivatives with this amine under anhydrous conditions led to the formation of the corresponding ureas; *i.e.*, cleavage of either the Si–N or Si–Si linkages did not occur.



$$OCN\text{-}(R)_2SiSi(R)_2\text{-}NCO + HN\text{-}(CH_2)_4\text{-}CH_2 \longrightarrow CH_2\text{-}(CH_2)_4\text{-}N\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}(R)_2SiSi(R)_2\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}N\text{-}(CH_2)_4\text{-}CH_2$$

$R = CH_3$ or C_6H_5

This result establishes that these materials react as difunctional isocyanates under anhydrous conditions. It therefore should be possible to incorporate the tetraorganodisilane unit into polymeric systems by reaction through these isocyanate linkages. Investigations are under way to explore this possibility.

Experimental Section

Reagents.—(a) The nitrogen used was first bubbled through an alkaline solution of pyrogallol (15 g of pyrogallol dissolved in 100 ml of 50% sodium hydroxide solution) and then through concentrated sulfuric acid followed by passage through a solid sodium hydroxide–Drierite trap.

(b) The piperidine was stored over potassium hydroxide for at least 2 days before distillation from fresh potassium hydroxide.

(c) The solvents were placed over an appropriate drying agent (calcium chloride was used in most cases) and distilled from fresh drying agent. The solvents were then deoxygenated by allowing deoxygenated anhydrous nitrogen gas to bubble through them for at least 1 hr.

---

[1] Abstracted in part from the M.S. Thesis of E. B. Moynahan, Lowell Technological Institute, 1965.

[2] To whom inquires should be addressed: Merrimack College, North Andover, Mass. 01845.

[3] R. G. Neville and J. J. McGee, *Can. J. Chem.*, **41**, 2123 (1963), and references contained therein.

[4] J. Goubeau and E. Henbach, *Ber.*, **93**, 1117 (1960).

[5] J. V. Urenovitch and A. G. MacDiarmid, *J. Chem. Soc.*, 1091 (1963).

[6] M. Kumada, M. Yamaguchi, Y. Yamamoto, S. Nakajima, and K. Shina, *J. Org. Chem.*, **21**, 1264 (1956).

[7] H. J. S. Winkler and H. Gilman, *ibid.*, **26**, 1265 (1961).