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# A Proton Magnetic Resonance Study of β-Diketone Diimine Schiff Bases and Some of Their Diamagnetic Metal Chelates

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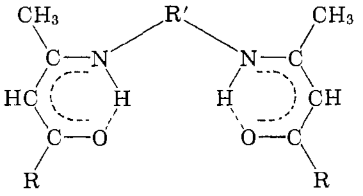
The proton magnetic resonance (pmr) spectra of acetylacetone, its palladium(II) and platinum(II) chelates, as well as 14 β-diketone diimine Schiff bases and several of their diamagnetic nickel(II), palladium(II), and platinum(II) chelates, are reported. The spectra indicate that all of the ligands studied exist mainly in the ketamine form (I) and suggest that in the benzoylacetone diimine ligands Schiff base formation occurs at the acetyl rather than the benzoyl carbonyl. In general, replacement of two ligand protons by a metal atom causes only small changes in the spectrum of a compound. The spectra of the *meso* and *dl* forms of bis(acetylacetone)stilbenediimine differ significantly as do the spectra of their nickel(II) chelates. These differences are discussed in terms of steric effects and magnetic shielding effects arising from proximity of the phenyl groups to the neighboring protons. The relative resonance positions of the protons in II (R = $CH_3$, $CF_3$, and $C_6H_5$) are interpreted in terms of the inductive and/or resonance effects of R.

We here report a study of the proton magnetic resonance (pmr) spectra of 14 β-diketone diimine Schiff bases (I) and several of their diamagnetic Ni(II), Pd(II), and Pt(II) chelates. The study was undertaken to determine the effect of various substituents on the electron density distribution in these molecules, and especially the changes produced by metal chelation. The pmr spectra of four of the ligands have been reported by Dudek and Holm,[2] but none of the metal chelates has been thus far investigated by pmr spectroscopy. In addition to the Schiff bases and their chelates, acetylacetone and its Pd(II) and Pt(II) chelates were studied for purposes of comparison. Bis(acetylacetonato)nickel(II) was not considered, since it is paramagnetic.



I

R = $CH_3$, R′ = $CH_2CH_2$, $CH(CH_3)CH_2$, $CH_2CH_2CH_2$, *meso*- and *dl*-$CH(C_6H_5)CH(C_6H_5)$
R = $C_6H_5$, R′ = $(CH_2)_n$ ($n$ = 2, 3, 4, 5), $CH(CH_3)CH_2$, $CH_2CHOHCH_2$
R = $CF_3$, R′ = $CH(CH_3)CH_2$
R = *p*-$C_6H_4Br$, R′ = $CH(CH_3)CH_2$
R = *p*-$C_6H_4OCH_3$, R′ = $CH_2CH_2$

## Experimental Section

**Preparation of Compounds.**—The preparation and properties of most of the compounds used in this study have been reported elsewhere.[3,4] The remainder are given here.

Bis(acetylacetonato)palladium(II) was prepared according to the method of Grinberg and Simonova.[5] The compound was recrystallized from benzene to give fine, orange-yellow needles. The compound does not melt, but begins to darken at *ca.* 132°; decomposition appears complete at *ca.* 205°. Grinberg and Simonova found it to darken at 150° and decompose at 180°.

Bis(acetylacetonato)platinum(II) was prepared by a procedure similar to that used for the Pd(II) chelate. When heated, it began to sublime with decomposition at 230°. The compound was prepared by Professor David Todd at Clark University.

Bis(acetylacetone)trimethylenediimine was formed by adding to 10 ml (0.098 mole) of acetylacetone in 20 ml of petroleum ether (bp 30–60°) 4 ml (0.048 mole) of trimethylenediamine. The reactants were mixed slowly with constant stirring at 0°. The white product was filtered, recrystallized immediately from anhydrous ethyl ether, and vacuum dried for 1 hr at 0°. The compound prepared in this way melts at 50–52° (lit.[6] 51°; a melting point of 61° has also been reported[2]). The freshly prepared compound tends to turn to an oil very readily even when stored in the cold. When bis(acetylacetone)trimethylenediimine is prepared according to this procedure and then dissolved immediately in $CDCl_3$, its pmr spectrum shows no N–H···O absorption and differs in many other ways from the spectrum of the aged sample. The spectrum of the solution changes continually over a period of several weeks and gradually approaches that expected for the ketamine form (I). A sample of the compound which was several months old was recrystallized from petroleum ether and air dried (mp 51–51.5°). Its pmr spectrum was that expected for the hydrogen-bonded ketamine form (I), and it is the data for this form which are reported here.

Bis(acetylacetone)trimethylenediiminopalladium(II) and the following chelate were prepared by a modification of the procedure reported for bis(acetylacetonato)palladium(II).[5] A mixture of 7.1 mmoles of $PdCl_2$, 13.8 mmoles of the ligand, and 14 mmoles of KOH in 15 ml of $H_2O$ was refluxed for 1.25 hr. The chelate which formed was removed by filtration and recrystallized from acetone–water. The yield of orange-yellow crystals was 24%. The compound melts at 190–191°. *Anal.* Calcd for $C_{13}H_{20}O_2N_2Pd$: C, 45.54; H, 5.88. Found: C, 45.89; H, 6.03.

Bis(acetylacetone)propylenediiminopalladium(II) was prepared by refluxing for 1.5 hr a mixture of 7.1 mmoles of $PdCl_2$, 13.8 mmoles of the ligand, and 14.1 mmoles of KOH in 35 ml of $H_2O$. The compound was recrystallized from acetone–water to yield orange crystals which melt at 169–171°. *Anal.* Calcd for $C_{13}H_{20}O_2N_2Pd$: C, 45.54; H, 5.88. Found: C, 45.77; H, 6.02. The yield was only 7% by this method.

Bis(acetylacetone)stilbenediimine (*dl* and *meso* forms) and its Ni(II) chelates were kindly supplied by Ichiro Murase. The *meso* Schiff base was prepared by heating the diamine and acetylacetone in a 1:2 molar ratio without solvent and recrystallizing the

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[2] G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1961).

[3] P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *ibid.*, **77**, 5820 (1955).

[4] R. J. Hovey, J. J. O'Connell, and A. E. Martell, *ibid.*, **81**, 3189 (1959).

[5] A. Grinberg and L. Simonova, *Zh. Prikl. Khim.*, **26**, 880 (1953); *Chem. Abstr.*, **47**, 11060g (1953).

[6] A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, **5**, 170 (1958).

condensation product from methanol. The *dl* compound was prepared in a similar manner at room temperature and was recrystallized from cyclohexane. The nickel(II) chelates were prepared by heating the Schiff base with nickel acetate in methanol and recrystallizing the product from methanol. Details of the procedure and properties of the products will be reported elsewhere.[7]

Bis(acetylacetone)-*meso*-stilbenediimine: *Anal.* Calcd for $C_{24}H_{28}N_2O_2$: C, 76.60; H, 7.44; N, 7.44. Found: C, 76.69; H, 7.62; N, 7.46. Nickel(II) chelate: *Anal.* Calcd for $C_{24}H_{26}N_2O_2Ni$: N, 6.47. Found: N, 6.56.

Bis(acetylacetone)-*dl*-stilbenediimine: *Anal.* Calcd for $C_{24}H_{28}N_2O_2$: C, 76.60; H, 7.44; N, 7.44. Found: C, 76.52; H, 7.35; N, 7.52. Nickel(II) chelate: *Anal.* Calcd for $C_{24}H_{26}N_2O_2Ni$: N, 6.47. Found: 6.63.

Microanalyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Bis(*p*-methoxybenzoylacetone)ethylenediimine was prepared from *p*-methoxybenzoylacetone and ethylenediamine according to the procedure given for bis(benzoylacetone)ethylenediimine.[3] The Schiff base melts at 171–172.5°. The diketone had been prepared by a Claisen condensation of *p*-methoxyacetophenone with ethyl acetate. The diketone melts at 53–54°.

**Proton Magnetic Resonance Spectra.**—All spectra were recorded on a Varian A-60 spectrometer at 35°. The spectra are of 10% solutions of the compounds in $CDCl_3$, with tetramethylsilane (TMS) as the internal reference. The resonance positions are reported in $\tau$ units; $\tau$ is defined as $10.00 - \delta$, where $\delta$ is the chemical shift in parts per million (ppm) below the TMS signal. The spectrometer was calibrated daily by use of the mixture of liquids suggested by Jungnickel.[8] Accordingly, the reported resonances are expected to be accurate to $\pm 0.02$ $\tau$ unit or better in all cases, except for the $N-H\cdot\cdot O$ resonance. This latter absorption is beyond the range of the calibration mixture and, in addition, is a broad and often irregularly shaped peak. Somewhat lower accuracy must be claimed for its position. Band assignments are based on integrated band areas, assignments reported for similar groups, and analogies drawn from simpler compounds in the same series. Several integrations were made on each compound; these are discussed, however, only when necessary or helpful for the understanding of a particular band assignment.

## Results

The experimental results of this study are summarized in Table I. In the discussion, in addition to referring to the compounds by their number in Table I, we use the following abbreviations in naming them: Ac = acetylacetone (2,4-pentanedione); Bz = benzoylacetone (1-phenyl-1,3-butanedione); en = ethylenediamine; pn = propylenediamine (1,2-propanediamine); tri = trimethylenediamine (1,3-propanediamine); SDA = stilbenediamine (1,2-diphenyl-1,2-ethanediamine). Thus, for example, Ac(pn)Ni stands for bis(acetylacetone)propylenediiminonickel(II).

## Discussion

**Acetylacetonates. Pt Chelates.**—Bis(acetylacetonato)palladium(II) (no. 2, Table I) shows a sharp peak at $\tau$ 4.58 due to the proton in each chelate ring and another at $\tau$ 7.93 due to the four methyl groups. The analogous Pt(II) complex (no. 3) has a similar spectrum; each band is, however, accompanied by a doublet of lesser intensity owing to coupling of protons with $Pt^{195}$ (spin $^1/_2$). Both $Pt^{195}$–H couplings are through four bonds in this compound, but the Pt–ring proton coupling constant ($J$ = 10.6 cps) is considerably larger than the Pt–methyl proton coupling constant ($J$ = 4.8 cps). The stronger coupling in the former case may be due in part to resonance in the pseudo-aromatic chelate ring. These coupling constants agree well with those reported recently by Lewis, *et al.*[9]

In the spectrum of Ac(en)Pt (no. 7) each of the bands is also accompanied by a doublet due to $Pt^{195}$–H coupling. The Pt–ring proton coupling constant ($J$ = 5.3 cps) is smaller here than in the acetylacetone complex ($J$ = 10.6 cps), as is $J(Pt^{195}–CH_3)$, namely, *ca.* 3 cps as compared with 4.8 cps in bis(acetylacetonato)platinum(II) (no. 3). This may be an indication of less resonance in the six-membered chelate rings in Ac(en)Pt. In this chelate the four methyl groups form two magnetically nonequivalent pairs whose resonances are separated by 4.6 cps. The resolution attainable in the spectrum does not allow us to say whether there are actually two slightly different $Pt–CH_3$ coupling constants. The coupling constant between Pt and the diimine bridge protons ($J$ = 30.1 cps) agrees with values obtained for similar compounds: *e.g.*, $J$ = 32–34 cps in $[PtX_2L]$ (X = Cl, Br, I; L = $o$-$(CH_3)_2N$-$C_6H_4$-$P(C_6H_5)_2$ and similar ligands).[10] The part of the diimine bridge proton absorption which is due to the $Pt^{195}$–H pattern, 36%, is in reasonable agreement with the 33.7% expected from the natural abundance of $Pt^{195}$.

The pmr absorptions of acetylacetone (no. 1) are included for purposes of comparison. The assignments have been made by Reeves.[11] In the 10% (0.08 mole fraction) $CDCl_3$ solution studied here the compound was found to be 83.5 ± 0.5% enolized at 35°. This was determined by three integrations of the $CH_3$ (enol) and $CH_3$ (keto) peaks and three integrations of the $=CH-$ and $-CH_2$ peaks. It is clear that the resonance positions of the enol form do not shift appreciably upon chelation with a metal. This had been noted earlier by Holm and Cotton,[12] who concluded that the position of the $=CH-$ resonance in acetylacetonates seems to be independent of the metal's size, charge, or ability to $\pi$ bond to the ligand. There seems furthermore to be no correlation between the shifts they observed and the electronegativity of the metals.

**Ac(en) and Its Chelates.**—The three molecules, Ac(en)M (M = Ni, Pd, Pt) (no. 5–7), are presumably all isosteric and differ only in the nature of the metal. Analyses show the metal to be at most four-coordinated. While no X-ray studies of these compounds have been reported, the expectation is that all three are approximately square-planar and similar in structure to the analogous Cu(II) chelate. This latter has been shown[13] to be approximately planar, except for the *gauche* configuration of the ethylene bridge, and to be slightly concave toward the center. Likewise, Gurr[14] has

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(14) G. E. Gurr, *Inorg. Chem.*, **3**, 614 (1964).

TABLE 1

PMR DATA (IN τ UNITS) FOR 10% SOLUTIONS IN $CDCl_3$ AT 35° WITH TMS AS INTERNAL REFERENCE (COUPLING CONSTANTS, *J*, IN CPS)

| | Compound | $CH_3$ (diketone) | =CH— (diketone) | N-H··O | Terminal $CH_2$ and/or CH of bridge | (a) Bridge $CH_3$ (doublet); (b) $C_6H_5$; (c) central $CH_2$ of bridge; (d) other |
|---|---|---|---|---|---|---|
| (1) | Acetylacetone (enol)[a] | 7.96 | 4.49 | | | (d) O-H··O at −5.29 |
| (2) | Bis(acetylacetonato)palladium(II) | 7.93 | 4.58 | | | |
| (3) | Bis(acetylacetonato)platinum(II) | 8.05 ($J_{Pt-H}$ = 4.8) | 4.49 ($J_{Pt-H}$ = 10.6) | | | |
| (4) | Bis(acetylacetone)ethylenediimine | 8.00, 8.08[k] | 5.00 | −0.84 | 6.58[f] | |
| (5) | Bis(acetylacetone)ethylenediiminonickel(II) | 8.13 | 5.10 | | 6.93 | |
| (6) | Bis(acetylacetone)ethylenediiminopalladium(II) | 7.98, 8.03[k] | 5.14 | | 6.56 | |
| (7) | Bis(acetylacetone)ethylenediiminoplatinum(II) | 8.09, 8.17[k] ($J_{Pt-H}$ = *ca.* 3) | 5.07 ($J_{Pt-H}$ = 5.3) | | 6.55 ($J_{Pt-H}$ = 30.1) | |
| (8) | Bis(acetylacetone)propylenediimine | 8.00, 8.09,[k] 8.12[k] (ratio 2:1:1) | 5.02, 5.04 | −0.89[b] | 6.72[c] | (a) 8.73 (*J* = 6.4) |
| (9) | Bis(acetylacetone)propylenediiminonickel(II) | 8.14[e] | 5.11, 5.15 | | 7.29[d] | (a) 8.69 (*J* = 6.9) |
| (10) | Bis(acetylacetone)propylenediiminopalladium(II) | 7.99, 8.01,[k] 8.05[k] (ratio 2:1:1) | 5.14, 5.17 | | 6.86[d] | (a) 8.78 (*J* = 6.6) |
| (11) | Bis(acetylacetone)trimethylenediimine | 8.00, 8.07[k] | 5.01 | −0.85 | (6.64 (*J* = 6.3) (quartet) | (c) 8.13 (*J* = 6.2) |
| (12) | Bis(acetylacetone)trimethylenediiminopalladium(II) | 8.02 | 5.15 | | 6.95 (irreg triplet) | (c) Overlaps $CH_3$ (diketone) |
| (13) | Bis(acetylacetone)-*dl*-stilbenediimine | 7.97, 8.20[k] | 5.01 | −1.73 (*J* = 6.9) | 5.28[f] | (b) 2.86[g] |
| (14) | Bis(acetylacetone)-*dl*-stilbenediiminonickel(II) | 8.07, 8.50[k] | 5.14 | | 5.81 | (b) 1.70, 2.60[h] |
| (15) | Bis(acetylacetone)-*meso*-stilbenediimine | 7.98, 8.32[k] | 5.03 | −1.47 (*J* = 7.6) | 5.14[f] | (b) 2.76[g] |
| (16) | Bis(acetylacetone)-*meso*-stilbenediiminonickel(II) | 8.11, 8.47[k] | 5.13 | | 5.34 | (b) 2.44, 2.96[h] |
| (17) | Bis(trifluoroacetylacetone)propylenediimine | 7.95[i] | 4.65, 4.67 | −1.18[b] | 6.49[c] | (a) 8.63 (*J* = 6.4) |
| (18) | Bis(trifluoroacetylacetone)propylenediiminonickel(II) | 7.97, 8.02 | 4.55, 4.60 | | 7.18[d] | (a) 8.62 (*J* = 6.5) |
| (19) | Bis(benzoylacetone)ethylenediimine | 7.95 | 4.31 | −1.51 | 6.46[f] | (b) 2.16,[j] 2.61[j] |
| (20) | Bis(benzoylacetone)ethylenediiminonickel(II) | 8.01 | 4.36 | | 6.88 | (b) Position not determined because of low solubility |
| (21) | Bis(benzoylacetone)propylenediimine | 7.97, 8.00 | 4.34[b] | −1.62[f] | 6.63[c] | (a) 8.67 (*J* = 6.3); (b) 2.15,[j] 2.62[j] |
| (22) | Bis(benzoylacetone)propylenediiminonickel(II) | 8.02, 8.06 | 4.36, 4.40 | | 7.24[d] | (a) 8.64 (*J* = 6.4); (b) 2.23,[j] 2.69[j] |
| (23) | Bis(benzoylacetone)trimethylenediimine | 7.95 | 4.32 | −1.39 | 6.55 (*J* = 6.3) (quartet) | (b) 2.17,[j] 2.62;[j] (c) multiplet which overlaps diketone $CH_3$ |
| (24) | Bis(benzoylacetone)-1,3-diiminopropanol-2 | 8.07 | 4.40 | −1.43 (*J* = 5.5) (triplet) | 6.61 (*J* = 5.7) (triplet) | (b) 2.22,[j] 2.63;[j] (d) OH at 4.68; CH (bridge) at 6.02[j] (*J* ~ 5.5) |
| (25) | Bis(benzoylacetone)-1,4-butanediimine | 7.97 | 4.33 | −1.47[b] | 6.66[f] | (b) 2.14,[j] 2.61;[j] (c) 8.25[f] |
| (26) | Bis(benzoylacetone)-1,5-pentanediimine | 7.97 | 4.35 | −1.48[b] | 6.71[f] | (b) 2.14,[j] 2.63;[j] (c) 8.39[b] |
| (27) | Bis(*p*-bromobenzoylacetone)-propylenediimine | 7.95, 7.99 | 4.39 | −1.61[f] | 6.60[c] | (a) 8.63 (*J* = 6.2); (b) $\nu_A$ = 2.29, $\nu_B$ = 2.49 |
| (28) | Bis(*p*-bromobenzoylacetone)-propylenediiminonickel(II) | 8.00, 8.05 | 4.40, 4.44 | | 7.22[d] | (a) 8.63 (*J* = 6.4); (b) $\nu_A$ = 2.38, $\nu_B$ = 2.57 |
| (29) | Bis(*p*-methoxybenzoylacetone)-ethylenediimine | 7.98[b] | 4.36 | −1.33 | 6.50[f] | (b) $\nu_A$ = 2.18, $\nu_B$ = 3.13; (d) *p*-$OCH_3$ at 6.19[b] |

[a] Keto resonances: $CH_3$, τ 7.77; $CH_2$, τ 6.42. [b] Unresolved multiplet. [c] Center of triplet at high-field end of a complex multiplet which extends over *ca.* 0.9 ppm. [d] Prominent peak near high-field end of a complex multiplet which extends over *ca.* 1.0 ppm. [e] Four peaks visible over τ 0.05 range. [f] Complex multiplet. [g] Tallest peak in multiplet. [h] See Figure 1. [i] Doublet, Δν = 0.9 cps. [j] Center of multiplet. [k] Higher field signal(s) due to $CH_3$ groups adjacent to diimine bridge.

shown from X-ray data that the Cu(II), Ni(II), and Pd(II) chelates of 4-amino-3-penten-2-one are all isomorphous. Because Pd(II) usually forms square-planar complexes, he concludes that all three chelates have a square-planar structure.

In these three compounds, Ac(en)M, as in metal acetylacetonates,[12,15] there seems to be no general correlation between the proton chemical shifts and the radius of the metal atom or the sum of the first and second ionization potentials or the electronegativity of the metal. A comparison of acetylacetone (no. 1) and its Pd and Pt chelates and of Ac(en) (no. 4) and its Pd and Pt chelates, however, indicates that the same

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(15) J. Smith and J. Thwaites, *Discussions Faraday Soc.*, **34**, 143 (1962).

trends operate in each set. Of all the protons in the molecule, the =CH– resonance in Ac(en)M is least sensitive and that of the bridge methylene groups most sensitive to the nature of M. These effects may be due in part to a changing of the geometry of the ligand as the metal atom is changed. The =CH– of the approximately planar six-membered ring would be least affected. The resonance of the ethylene bridge protons, on the other hand, might be quite noticeably changed by a substitution of Pt or Pd for Ni, the radii of the former two being about 10% larger than that of Ni. This could cause a lessening of the puckering of the ethylene bridge with consequent changes in the proton resonance. The methyl signal in Ac(en)Pd and Ac(en)Pt is a doublet. It is probable that the lower field signal is due to the methyls adjacent to the C–O groups, since these would be slightly less shielded than those near the C–N groups. In Ac(en)Ni the methyl signal is a singlet in $CDCl_3$; the expected two peaks appear when $CCl_4$ or pyridine is used as the solvent.

The =CH– resonance absorption in Ac(en) and its Pt and Pd chelates is at higher field ($\tau$ 5.00–5.14) than in the corresponding acetylacetone compounds ($\tau$ 4.49–4.58). This can be interpreted as an indication of poorer resonance in the six-membered Schiff base chelate ring, which results in less deshielding of the proton attached to the ring. It is of interest to note that in bis(thiobenzoylacetonato)nickel(II), which has two sulfur and two oxygen atoms bonded to the metal, the $CH_3$ and =CH– resonances appear at $\tau$ 7.69 and 2.93, respectively.[16] In Bz(en)Ni (no. 20) the corresponding resonances are at $\tau$ 8.01 and 4.36. If the explanation in terms of resonance is correct, this would indicate a considerable increase in resonance in the sulfur-containing chelate ring. This may in turn be connected among other things with the availability of d orbitals on the sulfur for bonding with the nickel.

**Palladium Chelates.**—The spectra of the three palladium chelates (no. 6, 10, 12) are all very much alike except for the resonances of the diimine bridge protons. The unusual triplet at $\tau$ 6.95 in the spectrum of Ac(tri)Pd (no. 12) is due to the two terminal $CH_2$ groups of the bridge; the integrated area indicates 3.9 protons. The separation between the two lower field peaks is 5.2 cps, and between the two higher field peaks, 5.0 cps; the relative heights of the peaks from lower to higher field are 1:1.3:1.6. A triplet would be expected for this absorption, but not in the form observed. The reason for the shape is not known.

**Acetylacetone–Stilbenediimine Compounds.**—The two isomeric ligands, *dl*- and *meso*-AcSDA (no. 13, 15) differ only in the spatial arrangement of the protons and phenyl groups on the diimine bridge. The *meso* form has a plane of symmetry perpendicular to the C–C bridge bond. The *d* and *l* forms contain no such plane, but are mirror images of each other. All resonance and inductive effects in the two compounds are expected, to a first approximation, to be the same, and the pmr spectral differences should be ascribed to steric and magnetic shielding effects arising mainly from the phenyl groups. Molecular models indicate that the methyl groups nearest the bridging group are in both isomers near the $\pi$ clouds of the adjacent phenyl groups. This causes a diamagnetic shielding of the protons of these methyl groups and an upfield shift of their resonance. Since several conformers are possible for each isomer, it may be that in the *dl* form these methyl groups are on the average farther from the phenyl groups and so less affected by the $\pi$ cloud than is the case in the *meso* form. The result would be that the methyl resonance signal appears at slightly lower field in the *dl* form ($\tau$ 8.20) than in the *meso* ($\tau$ 8.32), but in both cases at higher field than in Ac(en) (no. 4) ($\tau$ 8.08). In both AcSDA isomers the higher field methyl signal is broader and slightly less intense than the other methyl signal. This may be an indication of some restriction of rotation of the methyl groups which are near to the bulky phenyl groups. Molecular models also indicate that each N–H··O proton in these ligands lies very close to the plane of the nearest phenyl group and so would experience a deshielding similar to but weaker than that felt by protons attached directly to the phenyl ring.[17] The N–H··O resonance is at $\tau$ −0.84 in Ac(en) and at $\tau$ −1.47 and −1.73, respectively, in *meso*- and *dl*-AcSDA. Presumably the effect is more noticeable in the *dl* isomer; the large number of possible conformers would, however, make this impossible to predict.

The bridge methylene groups in Ac(en) resonate at $\tau$ 6.58. Replacement of protons by phenyl groups causes the signal of the remaining bridge protons to appear at *ca.* $\tau$ 5.2. The difference in resonance between the *dl* ($\tau$ 5.28) and *meso* ($\tau$ 5.14) forms can probably again be explained as an effect of differences in proximity of the proton to the $\pi$ cloud of the phenyl group on the adjacent carbon atom.

A complex pattern appears for the resonance of the bridge protons in both isomers of AcSDA (Figure 1a). The pattern is due to spin–spin coupling, since at 100 Mcps the spacings within the multiplet remain unaltered. The pattern was also shown to be due to coupling of the bridge protons with the NH protons; this was done by irradiation of the *dl* isomer at a frequency corresponding to the absorption at $\tau$ −1.73 (due to N–H··O). This decoupled the CH resonance from that of the NH groups and the multiplet collapsed to a sharp singlet, whose position coincided with the midpoint of the complex multiplet. The resonance pattern accordingly seems to be due to virtual coupling[18] of the CH resonance with that of both hydrogen-bonded protons, which are bonded directly to the nitrogen atoms. A similar situation has been noted in Ac(en) by Dudek and Holm.[2]

In *dl*- and *meso*-AcSDANi (no. 14, 16) two methyl resonances appear, one at approximately the same

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[16] E. Bidell and P. J. McCarthy, unpublished results.

[17] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 180–182.

[18] J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

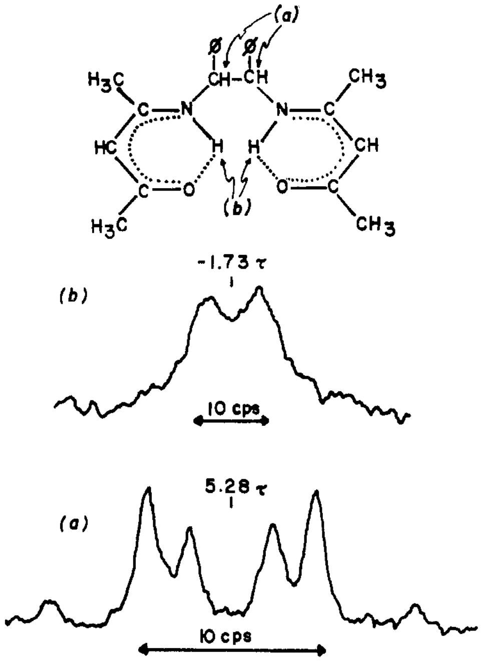

Figure 1.—Proton resonances of a 10% solution in $CDCl_3$ of bis(acetylacetone)-*dl*-stilbenediimine: (a) CH of the bridging group; (b) N–H · · · O proton.

position as in Ac(en)Ni (no. 5) and the other at higher field (*ca.* τ 8.5). The reason for the upfield shift of the latter is the same as that offered in the case of the free ligands, but the effect is more pronounced in the case of the metal chelates. The steric arrangements of the latter are more rigid, and, with no rotation possible about the bridge C–C bond, the phenyl and methyl groups are forced into positions very close to one another. The diamagnetic shielding effect on the methyl groups in the chelates is thus intensified. In these chelates the protons of the bridge resonate at a much lower field than the $CH_2$ in Ac(en)Ni, partly because each proton lies rather close to the plane of the phenyl group bonded to the same carbon atom. It is interesting to note, however, the rather large difference between the two isomers. In the *meso* isomer the two bridge protons are adjacent to one another and rather removed from any diamagnetic shielding effect of the phenyl groups. In the *dl* isomer, on the other hand, each proton is rather strongly shielded by the π cloud of the phenyl group on the next carbon; the resonance accordingly moves upfield by 0.47 ppm. The two protons in a given isomer are magnetically equivalent, for in each case they give a single absorption peak. The phenyl resonances of these two chelates are shown in Figure 2. The somewhat unexpected shapes and separations of the multiplets are again most probably due to mutual shielding effects of one phenyl group on the protons of the other; detailed analysis, however, does not seem feasible.

**Benzoylacetone–Diimine Compounds.**—The spectra of the six bis(benzoylacetone)diimine ligands (no. 19, 21, 23–26) are, as expected, quite similar except for the proton resonances of the bridging groups. The terminal methylene groups of the bridge appear at τ 6.46–6.71; central $CH_2$ groups resonate at higher field (*ca.* τ 7.9–8.4). Proximity to the electronegative nitrogen atom would cause the lower field resonance in the former case. One general trend is clearly observable. The signal for the terminal $CH_2$ groups of the bridge moves upfield as the length of the carbon chain of the bridge increases. This is noted also for Ac(en), Ac(tri), and their palladium chelates. It appears that the electron-withdrawing power of the nitrogens on the terminal methylene groups is extenuated with the addition of each methylene to the bridging group.

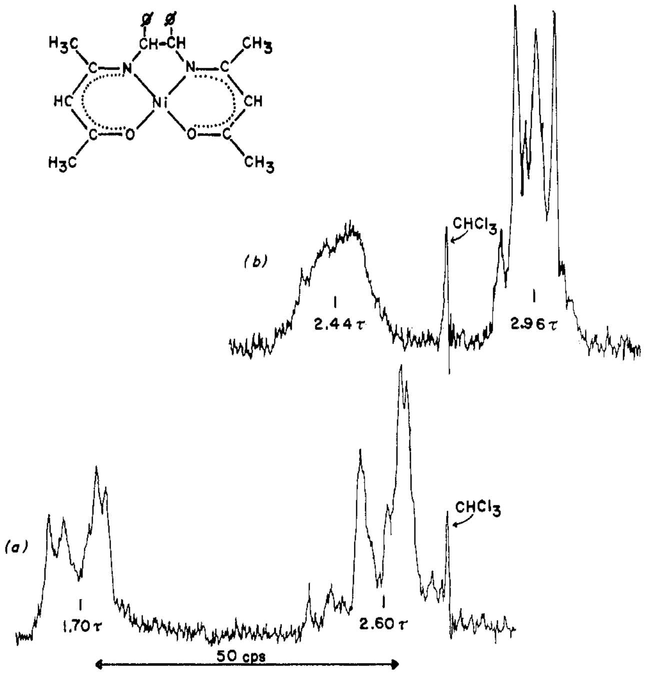

Figure 2.—Phenyl proton resonances of 10% solutions in $CDCl_3$ of bis(acetylacetone)stilbenediiminonickel(II): (a) *dl* isomer; (b) *meso* isomer.

Substitution of the methoxy group for the *p*-hydrogen in Bz(en) causes all the resonances to move upfield by 0.03 to 0.18 ppm. Since the over-all effect of methoxy substitution on a benzene ring is one of electron donation, the greater shielding of all the protons in the molecule and the ensuing upfield shift of the proton resonances is expected. It is of interest to note that both methyl signals in the spectrum of *p*-methoxy Bz(en) (no. 29) appear as unresolved multiplets owing to long-range coupling. That of the *p*-methoxy group is clearer, possibly due to a more efficient coupling of the methyl proton spins with those of the phenyl protons through the π cloud of the benzene ring.

Two of the ligands and one of the chelates discussed here contain *para*-substituted phenyl groups. The $A_2B_2$ pattern for the phenyl hydrogens was analyzed according to the method suggested by Anderson and McConnell.[19] $|\nu_A - \nu_B|$ was found to be 12.2, 11.3, and 56.7 cps, respectively, for *p*-bromo Bz(pn), its nickel chelate, and *p*-methoxy Bz(en). The chemical shifts reported in Table I (no. 27–29) are based on these calculated values.

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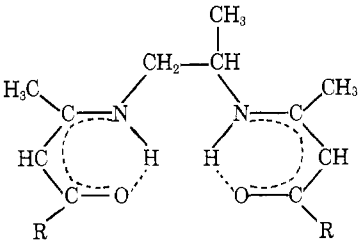
(19) W. A. Anderson and H. M. McConnell, *J. Chem. Phys.*, **26**, 1496 (1957); *cf.* also J. Parello, *Bull. Soc. Chim. France*, 2052 (1964).

**Substitution Effects.**—When the two terminal methyl groups in Ac(en) (no. 4) are replaced by two phenyl groups (no. 19), all of the resonances are shifted downfield. The effect is most noticeable in the resonances of those protons which are part of the chelate ring (N–H··O) or directly attached to the chelate ring (=CH–). Each of them is shifted *ca.* 0.7 ppm; the other signals are lowered about 0.1 ppm. The same effect is also noticed in the nickel chelates of these ligands, as well as in Ac(pn) (no. 8), Bz(pn) (no. 21), and their nickel chelates. A comparison of Ac(pn) and its trifluoro analog (no. 17) indicates that fluorine substitution also causes all resonances to shift downfield by about 0.1–0.4 ppm. The effect is again most noticeable in the protons which are part of or directly attached to the chelate ring.

The effect of $CF_3$ substitution as compared with that of $C_6H_5$ substitution (Table II) indicates that the $CF_3$ group causes greater downfield shifts than the phenyl groups for the methyl and bridge protons. This is in keeping with the greater inductive effect of the $CF_3$ group. The opposite effect is observed for the protons attached to, or part of, the chelate ring; here phenyl substitution causes greater downfield shifts than $CF_3$ substitution. This may be due to the fact that the phenyl groups can resonate with the pseudo-aromatic chelate ring and in this way make a significant contribution to the deshielding of the protons on the latter ring. This resonance is not possible for $CF_3$. The resonance and inductive effects are thus quite clearly separable here. A comparison of compounds no. 9, 18, and 22 in Table I shows that the trends operate also in the spectra of the nickel chelates of these ligands.

Table II

Effects of Substituents on Pmr Spectra[e]



| | R | | |
|---|---|---|---|
| | $CH_3$ | $CF_3$ | $C_6H_5$ |
| $CH_3$ (diketone) | 8.09, 8.12 | 7.95[d] | 7.97, 8.00 |
| $CH_3$ (bridge)[a] | 8.73 | 8.63 | 8.67 |
| $CH_2CH$ (bridge)[b] | 6.72 | 6.49 | 6.63 |
| CH (diketone) | 5.02, 5.04 | 4.65, 4.67 | 4.34[c] |
| N–H··O[c] | −0.89 | −1.18 | −1.62 |

[a] Doublet, $J$ = 6.3–6.4 cps. [b] Center of triplet at high-field end of complex multiplet. [c] Unresolved or complex multiplet. [d] Doublet, $\Delta\nu$ = 0.9 cps. [e] Resonances reported in $\tau$ units.

**pn-Bridged Compounds. Position of Schiff Base Formation.**—The introduction of a methyl group into the diimine bridge of a Schiff base or its chelate brings steric and magnetic asymmetry into the molecule. This is reflected in the diketone =CH– signal, which appears as a doublet, in some cases not well resolved, but in others clearly resolved with a separation up to 2.6 cps. The asymmetry also causes a splitting of the diketone methyl signal. In the spectrum of Ac(pn) (no. 8) and its chelates three peaks appear (relative intensities 2:1:1), one of which is an unresolved doublet. In the benzoylacetone derivatives, two clearly resolved methyl absorptions appear. This clear resolution is possibly an indication that the methyl groups are adjacent to the diimine bridge, where the effect of substitution on the bridge would be more strongly felt. Dipole moment measurements on metal chelates of Schiff bases formed from trifluoroacetylacetone, *p*-bromobenzoylacetone, or *m*-nitrobenzoylacetone have shown that the methyl groups are adjacent to the diimine bridge.[20,21] Nmr studies have also shown that benzoylacetone and primary amines react at the acetyl rather than the benzoyl carbonyl group.[22] The same then may be assumed to be true for unsubstituted benzoylacetone Schiff bases. The great similarity of the complete pmr spectra of Bz(pn)Ni (no. 22) and the *p*-bromo analog (no. 28) confirms this argument. The conclusion expressed earlier[23] that the phenyl groups are adjacent to the bridge in Bz(en) (no. 19) should be corrected in light of this discussion.

In Table I the values given for the $CH_2CH$ absorption of the pn-bridged ligands refer to the center of an irregular triplet which occurs in all of the spectra at the high-field end of a complex pattern. This point of reference allows comparison of chemical shifts. Likewise, the values reported for the metal chelates refer to one predominant peak which appears in all of the spectra toward the high-field end of the complex pattern. Again, it is given simply as a point of reference in comparing chemical shifts. The resonance for the propylene methyl in these ligands and chelates appears as a doublet ($J$ = 6.2–6.9 cps) at $\tau$ 8.6–8.7; the first-order splitting is caused by the adjacent CH group.

**Trimethylene-Bridged Compounds.**—The resonance absorptions in the spectrum of Ac(tri) (no. 11) have been assigned by Dudek and Holm.[2] In Bz(tri) (no. 23) the central $CH_2$ of the bridge appears as a multiplet which overlaps the strong $CH_3$ resonance at $\tau$ 7.95. The former should appear as a quintet as does the corresponding group in 1,3-dichloropropane ($\tau$ 7.80, $J$ = 6.2 cps) or trimethylene oxide ($\tau$ 7.28, $J$ = 7.5 cps).[24] Here, however, only three or four of the five bands can be seen, and the separation is about 6.7–7.0 cps. The two terminal $CH_2$ groups of the bridge are equivalent and appear as a normal quartet at $\tau$ 6.55 ($J$ = 6.3 cps). If we assume that the enolic hydrogen is bonded to the nitrogen, the signal of the terminal methylene would be split into a triplet by the central $CH_2$ and further split into a doublet by the NH proton. The observed quar-

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[20] P. J. McCarthy and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 2106 (1956).

[21] R. J. Hovey and A. E. Martell, *ibid.*, **82**, 2697 (1960).

[22] G. O. Dudek and E. P. Dudek, *ibid.*, **86**, 4283 (1964).

[23] P. J. McCarthy and A. E. Martell, *ibid.*, **78**, 264 (1956).

[24] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Vol. I, Varian Associates, Palo Alto, Calif., 1962, Spectra No. 31, 33.

tet would result if the two triplets overlap, which in turn would occur if $J(CH_2–CH_2) = J(CH_2–NH)$. Since the broad N–H··O resonance in Bz(tri) ($\tau$ −1.39) shows no splitting, this hypothesis is not verifiable from the spectrum of this compound. In the spectrum of the Bz 1,3-diiminopropanol-2 (no. 24), however, the N–H··O resonance appears at $\tau$ −1.43 as a triplet ($J$ = 5.5 cps) owing to coupling with the bridge methylene groups. In this compound the $CH_2$ resonance is also a normal triplet ($J$ = 5.7 cps), and the bridge CH resonance seems to be the expected quintet ($J \sim$ 5.5 cps). Accordingly, we may assume that the $CH_2$ signal is split into a doublet by both the NH and the CH protons and that the two doublets approximately overlap to give a 1:2:1 triplet, since all of the coupling constants are so nearly the same. Treatment of a $CDCl_3$ solution of this compound with two portions of $D_2O$ caused complete deuteration of the N–H··O proton, as evidenced by the disappearance of the absorption peak. The signal for the terminal $CH_2$ groups of the bridge was now split only by the adjacent CH proton, and the resulting unsymmetrical doublet ($J$ = 5.6 cps) appeared at the same position as the triplet in the nondeuterated compound.

**N–H··O Resonance.**—All of the Schiff base ligands investigated appear to be almost completely enolized in $CDCl_3$ solution. All show a broad band at about $\tau$ −0.8 to −1.7 owing to the N–H··O proton. In some cases the band is featureless, but in others splitting is clearly discernible, and in a few cases the splitting is clear enough to enable the coupling constant to be determined accurately (see Figure 1b). Undoubtedly the explanation of the splitting offered by Dudek and Holm[2] is the correct one, namely, that the enol proton is directly attached to the nitrogen and the splitting is due to coupling with the bridge protons. In acetylacetone the O–H··O resonance appears at $\tau$ −5.29. The shift to lower field compared with the resonance of N–H··O may be another indication of better resonance in the symmetrical acetylacetonate ring.

**Acknowledgment.**—The authors wish to thank Professors David Todd and Ichiro Murase and Mr. Edward Maslowsky for the preparation of several of the compounds used. Thanks are also due to Professor James Van Verth and Dr. James Colson for many helpful discussions, and also to the latter for running a spectrum at 100 Mcps.

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# The Stereochemistry and Preparation of Triethylenetetramine-Disubstituted Cobalt(III) Complexes

BY A. M. SARGESON AND G. H. SEARLE

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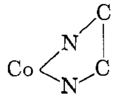
The preparation and resolution of some of the *cis*- and *trans*-$[Co(trien)X_2]^{n+}$ isomers [trien = triethylenetetramine; X = Cl, $OH_2$, $NO_2$; 2X = $CO_3$] are described. The relative stabilities and stereochemical detail are discussed in terms of the directing influences prescribed by the secondary NH groups and the nonbonding interactions between the possible conformers.

## Introduction

Although some work has been carried out on the preparation of cobalt(III) triethylenetetramine compounds,[1-4] little is known about the detailed structures of the complexes isolated. This paper concerns the preparation and isolation of isomers of several disubstituted cobalt(III) trien complexes and the assignment of their stereochemical form. It will be followed by papers describing the reactivity of the isomers.

The possible modes of wrapping the triethylenetetramine ligand ($NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ = trien) about a cobalt(III) ion are given in Figure 1. However, in addition to these topological isomers, several isomeric possibilities arise from the manner in which the secondary N atoms coordinate. For example the *trans*-$[Co(trien)X_2]^{n+}$ ion has three possible forms, Figure 2. All three conformations and configurations may be stable in slightly acidic solutions as interconversion and conformational interchange cannot occur in the *l*-, *d*-, and *meso-trans* isomers unless the secondary N protons dissociate. The *meso* configuration requires at least the central coordinated en unit to be in the envelope conformation



which is observed in some cyclopentane systems but which is not common in M–en chelates. The optically active *trans* isomers however have the usual staggered arrangement of the Co–en rings. Recently the active *trans* isomer has been prepared and its optical proper-

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[1] F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).

[2] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

[3] B. Das Sarma and J. C. Bailar, *J. Am. Chem. Soc.*, **77**, 5480 (1955).

[4] J. Selbin and J. C. Bailar, *ibid.*, **82**, 1524 (1960).