nate[17] cobalt(II) complexes. Octahedral complexes are ruled out on the grounds that a large orbital contribution is expected in the ground state which should cause $\mu_{eff}$ to fall in the range 4.8–5.6 BM.[16]

Near-infrared–visible spectra in the form of Nujol mulls have been measured and the observed absorption maxima are shown in Table III. Three and sometimes four bands are observed for each complex depending upon whether the broad band around 10,000 $cm^{-1}$ is split into two components. The similarity between the visible spectra of Co(XSALDAES) and those spectra of known tetrahedral complexes is very striking. The band around 10,000 $cm^{-1}$ is assigned to $^4A_2 \rightarrow {}^4T_1$ (F). The shoulder observed near 18,000 $cm^{-1}$ is assigned to $^4A_2 \rightarrow {}^4T_1$ (P).[18] In some of the complexes both bands are split into two components. The splitting probably arises in each case from the less than perfect $T_d$ symmetry that is anticipated for these materials. Bis(*N*-phenylsalicylaldiminato)cobalt(II) has been shown by spectral as well as crystallographic evidence to have a pseudotetrahedral geometry.[19,20] The electronic spectrum of this complex exhibits absorption bands at 7600, 10,700, 16,700 (sh), and 19,230 $cm^{-1}$. These band positions are in good agreement with those obtained for Co(XSALDAES)·$n$H$_2$O and also those obtained for *N,N'*-bis(salicylidene)polymethylenediaminocobalt(II) containing four to six methylene groups.[4] Since the spectra of hydrated and anhydrous Co(XSALDAES) are identical, it is most probable that a molecule of water is not coordinated to the metal in the solid state.

Absorption maxima from spectral measurements in chloroform are listed in Table III for some of the complexes. The similarity between solution and solid-state spectra is very striking which suggests that the tetrahedral geometry is maintained even in solution. Most of the complexes were also studied in *N,N*-dimethylformamide and similarly placed band maxima were found. As further evidence for a tetrahedral assignment, the intensities of the $\nu_2$ and $\nu_3$ bands are in the reported range for known tetrahedral complexes.[10,19]

By way of comparison the spectra of similar known five-coordinate, high-spin[21] and low-spin square-planar[10] cobalt(II) complexes are in disagreement with what we have observed for Co(XSALDAES).

The adoption of a pseudotetrahedral geometry instead of a square-planar or five-coordinate one as observed in the nickel(II) case supports the crystal field idea that for flexible polydentate ligands cobalt(II) forms more stable tetrahedral complexes than nickel(II). It also would appear from these results that the thioether linkage is insignificant concerning influencing the overall adopted structure. No doubt the low affinity of thioethers for first-row metals contributes to this observation although the restricting nature of the five-atom chain which contains the thioether group may prohibit a fifth coordination position to be spanned. The interaction of cobalt(II) with other dianionic pentadentate ligands is presently under way.

**Registry No.** Co(HSALDAES), 38402-75-4; Co(5-BrSALDAES), 38402-76-5; Co(5-CH$_3$SALDAES), 38402-77-6; Co[3-(CH$_3$)$_2$CHSALDAES], 38402-78-7; Co(5-NO$_2$SALDAES), 38402-79-8.

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[17] S. Yamada, *Coord. Chem. Rev.*, 1, 415 (1966).

[18] A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, p 329.

[19] L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Amer. Chem. Soc.*, 82, 3246 (1962).

[20] E. Frasson and C. Panattoni, *Z. Kristallogr., Kristallgeometrie, Kristallophys., Kristallochem.*, 116, 154 (1961).

[21] C. Furlani, *Coord. Chem. Rev.*, 3, 141 (1967); C. R. Hare, "Spectroscopy and Structure of Metal Chelate Compounds," K. Nakamoto and P. J. McCarthy, Ed., Wiley, New York, N. Y., 1968, pp 73–155.

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## Studies of an Acetylacetone Complex of Zinc Perchlorate

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In recent years several workers have reported the preparation of transition metal complexes of acetylacetone in which the ligand coordinates without the loss of a proton, *i.e.*, as an electrically neutral ligand instead of an anion. Allred and Thompson,[1] using several $\beta$-diketones, reported adducts with group IV tetrahalides, while van Leeuwen has prepared acetylacetone adducts of nickel(II)[2] and magnesium(II)[3] perchlorates. Sutin, *et al.*, has reported kinetic evidence for the complexation of transition metal ions by thenoyltrifluoroacetone[4] and by acetylacetone.[5] A group of Japanese workers has reported an adduct of acetylacetone with CoBr$_2$[6] as well as the crystal structures of both Mn(Hacac)$_2$Br$_2$[7,8] and Ni(acHac)$_2$Br$_2$.[9] The crystal structures, as well as infrared evidence, show that acetylacetone can coordinate to transition metal ions in either the keto or enol form in the solid state. In solution the kinetic studies,[4,5] as well as the nmr spectra reported by van Leeuwen[3] for [Mg(acHac)$_2$(H$_2$O)$_2$]$^{2+}$, show that both tautomers of the ligand are present. The nmr studies of Allred and Thompson[1] show only the keto form for Sn(acHac)Cl$_4$ in CH$_2$Cl$_2$, but ir studies indicate some dissociation of this complex in CH$_2$Cl$_2$. In order to investigate this type of complex further and in an attempt to determine the factors which influence the keto–enol tautomerism, we have prepared the new complex [Zn(acHac)$_2$(H$_2$O)](ClO$_4$)$_2$ and examined its nmr spectrum in CD$_3$NO$_2$.

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[1] A. L. Allred and D. W. Thompson, *Inorg. Chem.*, 7, 1196 (1968).

[2] P. W. N. M. van Leeuwen, *Recl. Trav. Chim. Pays-Bas*, 87, 396 (1968).

[3] P. W. N. M. van Leeuwen and A. P. Praat, *Inorg. Chim. Acta*, 4, 101 (1970).

[4] M. R. Jaffe, D. P. Fay, M. Cefola, and N. Sutin, *J. Amer. Chem. Soc.*, 93, 2878 (1971).

[5] D. P. Fay, A. R. Nichols, Jr., and N. Sutin, *Inorg. Chem.*, 10, 2096 (1971).

[6] Y. Nakamura and S. Kawaguchi, *Chem. Commun.*, 716 (1968).

[7] We shall indicate the enol form of coordinated acetylacetone as Hacac to emphasize the replaceable proton on the end of the molecule and the keto form as acHac to designate that the replaceable proton is in the middle of the molecule, *i.e.*, on the methylene carbon.

[8] S. Koda, S. Ooi, H. Kuroya, Y. Nakamura, and S. Kawaguchi, *Chem. Commun.*, 280 (1971).

[9] S. Koda, S. Ooi, H. Kuroya, K. Isobe, Y. Nakamura, and S. Kawaguchi, *Chem. Commun.*, 1321 (1971).

## Experimental Section

**Synthesis.** **$[Zn(acHac)_2(H_2O)](ClO_4)_2$** was synthesized by the method of van Leeuwen.[2] Approximately 0.01 mol of $Zn(H_2O)_6(ClO_4)_2$ was mixed with 0.06 mol of acetic anhydride to produce $Zn(AcOH)_6(ClO_4)_2$.[10] The reaction, being highly exothermic, was carried out in an ice bath. Isolation of the $Zn(AcOH)_6(ClO_4)_2$ and the remaining portions of the synthesis were performed in a glove bag under an $N_2$ atmosphere to protect the hygroscopic products. $Zn(AcOH)_6(ClO_4)_2$ (0.01 mol) was dissolved in a mixture of 10 g of nitromethane and 4 g (0.04 mol) of acetylacetone, which had been previously dried over Linde 4A molecular sieve. Sodium-dried diethyl ether (100–125 ml) was added and crystallization of the product occurred after 0.5–12 hr. The product was suction filtered and washed with ether. In spite of all efforts to keep the reaction dry, the product was always found to contain at least 1 mol of $H_2O$. *Anal.* Calcd for $[Zn(C_5H_8O_2)_2(H_2O)](ClO_4)_2$: C, 24.87; H, 3.73. Found:[11] C, 24.99; H, 3.70.

**$[Zn(acHac)_2](ClO_4)_2$** was obtained by drying $[Zn(acHac)_2(H_2O)](ClO_4)_2$ in a vacuum desiccator over $P_2O_5$ for 2 months. *Anal.* Calcd for $[Zn(C_5H_8O_2)_2](ClO_4)_2$: C, 25.83; H, 3.44. Found:[11] C, 25.46; H, 3.68.

**$Zn(acac)_2$.** $Zn(acac)_2(H_2O)$ was prepared by the method of Rudolph and Henry and dehydrated to $Zn(acac)_2$.[12]

**Physical Measurements.** Conductivity measurements were made on approximately $10^{-3}$ *M* solutions of the compound in $CH_3NO_2$ using an Industrial Instruments, Inc., Conductivity Bridge, Model RC16B2. The cell constant was determined with a standard 0.001 *N* KCl solution.

Infrared spectra of $[Zn(acHac)_2(H_2O)](ClO_4)_2$, as both Nujol mulls and in KBr wafers, were obtained using a Beckman IR-10 infrared spectrophotometer.

Nmr spectra were obtained in nitromethane-$d_3$ on a Varian HA-100 spectrometer equipped with a V6040 temperature controller, using TMS as an internal reference.

Solutions of the hygroscopic $Zn(acHac)_2(ClO_4)_2$ were prepared in a molded Plexiglas drybox manufactured by Van Beek Industries and equipped with a Pall Trinity Micro Corp. HA air dryer unit. Solutions of $[Zn(acHac)_2(H_2O)](ClO_4)_2$ were prepared under $N_2$ in a Model X-17-17 I$^2$R polyethylene glove bag manufactured by Instruments for Research and Industry.

## Results and Discussion

A plot of equivalent conductance *vs.* $\sqrt{C}$ for $[Zn(acHac)_2(H_2O)](ClO_4)_2$ in $CH_3NO_2$ yielded a slope of 483, a value in the range characteristic of a 1:2 electrolyte in $CH_3NO_2$ as reported by Feltham and Hayter.[13]

Infrared spectra of $[Zn(acHac)_2(H_2O)](ClO_4)_2$, both as Nujol mull and in KBr pellets, showed the characteristic[2,14] perchlorate bands at 622, 943, 1070–1160 (b), and 2020 $cm^{-1}$ (w). Also observed were (1) a weak band at 530 $cm^{-1}$, attributed to the M-O stretch,[14] (2) a broad, strong band between 3300 and 3500 $cm^{-1}$, characteristic of $H_2O$, (3) C-H stretching bands between 2850 and 2920 $cm^{-1}$, (4) a variety of C-C, C-$CH_3$, and OH bands between 1245 and 1470 $cm^{-1}$, also seen in acac complexes,[14] and (5) a split band with peaks at 1700 and 1725 $cm^{-1}$ along with a slightly smaller band at 1620 $cm^{-1}$, due to carbonyl stretching.

The ir bands assigned to the $ClO_4^-$ ions are similar to those reported by van Leeuwen[2] for $[Ni(acHac)_3](ClO_4)_2$ and the fact that they are not split indicates that the perchlorate ions are not coordinated. This is in agreement with the conductance data which indicate dissociable $ClO_4^-$ anions, *i.e.*, not part of the coordination sphere of the metal ion.

Gibrov[15] and coworkers have performed normal-coordinate analysis and assigned the ir absorption bands in the carbonyl region for both the keto and enol forms of acetylacetone. They have assigned the bands observed at 1708 and 1728 $cm^{-1}$ to the symmetric and antisymmetric carbonyl stretches in the keto form of acetylacetone. The enol carbonyl stretches, which are coupled to C=C stretches, occur at 1620 $cm^{-1}$, and below 1500 $cm^{-1}$. Since free acetylacetone is known to exist in a 20% keto–80% enol equilibrium, the keto peaks around 1700 $cm^{-1}$ are much weaker than the enol peak at 1600 $cm^{-1}$. The carbonyl band for complexed acetylacetone occurs at 1693 $cm^{-1}$ in $Ni(acHac)_2Br_2$, which is known to contain only keto chelates, while in $Mn(Hacac)_2Br_2$, which is known to have enolic ligands,[8] the carbonyl peak is at 1627 $cm^{-1}$. The spectrum of $[Ni(acHac)_3](ClO_4)_2$[2] exhibits a very broad, strong band at 1700 $cm^{-1}$, indicative of the keto form of the ligand, as well as a shoulder at 1625 $cm^{-1}$, which may be evidence for a small amount of the enolic ligand. The equally intense bands at 1620 and 1700 $cm^{-1}$ in the spectrum of $[Zn(acHac)_2(H_2O)](ClO_4)_2$ indicate the existence of both enol and keto chelates in this complex in the solid state. The frequencies of the carbonyl stretching vibrations reported here are little different from those of free acetylacetone, similar to the results reported[2] for $[Ni(acHac)_3](ClO_4)_2$ and $[Ni(acHac)_2(H_2O)_2](ClO_4)_2$.

Figure 1 shows a series of nmr spectra of $[Zn(acHac)_2(H_2O)_x](ClO_4)_2$ with varying amounts of $H_2O$. The spectrum of $[Zn(acHac)_2(H_2O)](ClO_4)_2$, Figure 1d, is quite similar to that observed for $[Mg(acHac)_2(H_2O)_2](ClO_4)_2$[3] and by analogy the peaks are assigned as follows: −2.25 ppm (enol methyl), −2.56 ppm (keto methyl), −4.42 ppm (keto methylene), −5.46 ppm ($H_2O$), −5.82 ppm (enol methine). The assignment of the $H_2O$ signal is verified by the growth of that peak upon addition of $H_2O$. The overlap of the keto methylene peak with the solvent prevents an area comparison with the keto methyl peak. While a similar overlap of the methine peak with the $H_2O$ peak prevents an accurate comparison of the areas of the methine and enol methyl peaks, the ratio is close to the expected value of 1:6. Comparison of the chemical shifts with those for free acetylacetone (−1.83 ppm, enol methyl; −2.00 ppm, keto methyl; −3.63 ppm, keto methylene; −5.56 ppm, enol methine) shows that all peaks are shifted and thus both the keto and enol forms must be coordinated to the $Zn^{2+}$ ion. The influence of the $Zn^{2+}$ ion upon the chemical shifts has been discussed elsewhere.[3] Variable-temperature studies down to the freezing point of the $CD_3NO_2$ solutions show that there is little temperature dependence of the chemical shifts, except of course for $H_2O$. All sharp peaks remain sharp throughout the temperature range and the $H_2O$ peak sharpens as the temperature is lowered. The decrease in the line width of the $H_2O$ resonance seems to result from a decrease in the exchange rate of the enol hydroxyl protons with $H_2O$, because at −30° a small peak assigned to the hydroxyl proton appears between −14 and −16 ppm and sharpens with decreasing temperature.

In the spectrum of $[Zn(acHac)_2(H_2O)](ClO_4)_2$ in Figure 1d, the enol peak is about 7% of the total area due to methyl groups. As the compound is progressively dried the spectra show less water, as well as a decreasing amount of complexed enolic acetylacetone. For the carefully dried and prepared sample of $[Zn(acHac)_2](ClO_4)_2$, shown in Figure 1a, only the two keto peaks, at −2.56 and −4.45 ppm, in the ratio 3:1 are observed. The enol peak has all but disappeared, leaving only the slightest trace at −2.28 ppm, which could be due to trace amounts of $H_2O$ remaining. From this evidence we conclude that $H_2O$ is necessary in order for the enol form of

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(10) P. W. N. M. van Leeuwen and W. L. Groeveld, *Recl. Trav. Chim. Pays-Bas,* 87, 861 (1968).

(11) Analysis by Chemalytics, Inc., Tempe, Ariz.

(12) G. Rudolph and M. C. Henry, *Inorg. Syn.*, 10, 74 (1967).

(13) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(14) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1968, pp 107, 216–217.

(15) L. A. Gibrov, Yu. A. Zolotov, and M. P. Noskova, *Zh. Strukt. Chim.*, 2, 448 (1968); *J. Struct. Chem.* (*USSR*), 9, 378 (1968).

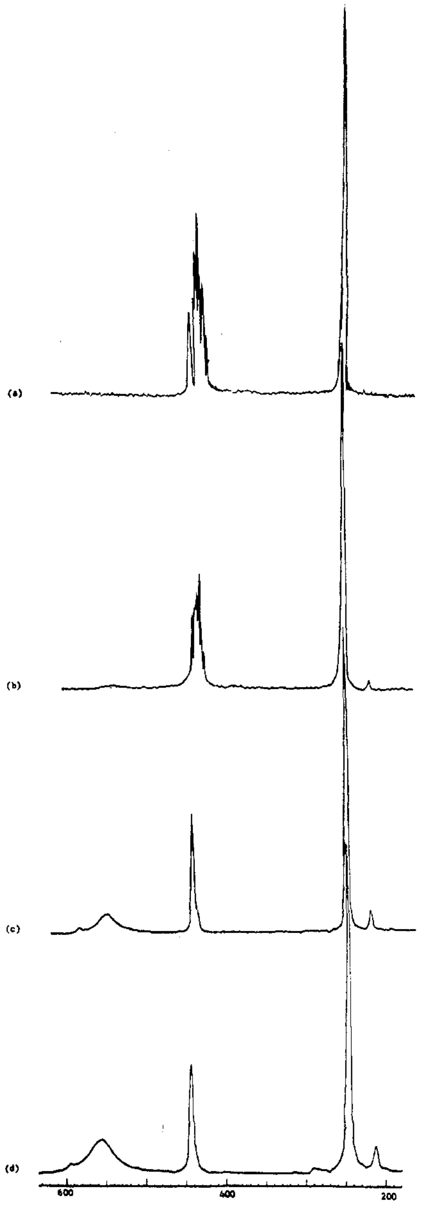

**Figure 1.** A series of pmr spectra of an acetylacetone complex of zinc perchlorate containing increasing amounts of water in $CD_3NO_2$: (a) $[Zn(acHac)_2](ClO_4)_2$, no water; (b) and (c), $[Zn(acHac)_2(H_2O)_x](ClO_4)_2$ where $0 < x < 1$; (d) $[Zn(acHac)_2(H_2O)](ClO_4)_2$.

the chelate to occur in solution. It is likely that in the solid state $[Zn(acHac)_2](ClO_4)_2$ exists as a pure keto chelate which reacts in solution to set up an equilibrium with the enol form. The Lewis base $H_2O$ acts as a proton carrier to transfer a proton from the methylene group of the keto chelate onto the carbonyl oxygen forming the enol hydroxy group and *vice versa.* The reaction between $H_2O$ and the hydroxy group is observed to be fast on the nmr time scale since only a single OH peak is observed at room temperature. On the other hand at all temperatures, separate keto and enol methyl peaks are observed, so that the exchange between them is slow on the nmr scale. Therefore the exchange between the keto methylene and $H_3O^+$ must be the slow step in the reaction, as would be expected.

If our hypothesis, that a Lewis base is necessary in order to establish an equilibrium between keto and enol complexes, is correct, then the addition of other bases to $[Zn(acHac)_2](ClO_4)_2$ should cause the appearance of the enol resonances. In our search to find such a base which would not decompose the complex, we settled upon $Zn(acac)_2$ which is the conjugate base of the $Zn(acHac)_2{}^{2+}$. Equimolar mixtures of $Zn(acHac)_2(ClO_4)_2$ and $Zn(acac)_2$ were prepared and dissolved in $CD_3NO_2$. The spectra show peaks at −2.11, −2.51, −4.34, and −5.70 ppm. The peak at −2.51 ppm would seem to be keto $CH_3$, with the keto $CH_2$ obscured by the solvent at −4.34 ppm. The remaining peaks must be due to $Zn(acac)_2$, and the area ratio of the peak at −2.11 ppm to that at −5.70 ppm is nearly 6:1. However, the chemical shifts of these peaks show a considerable shift from those of pure $Zn(acac)_2$ which has resonances at −2.00 ppm (methyl) and −5.47 ppm (methine).[16] Furthermore the area ratio of the "acac" methyl peak to that of the keto methyl peak is 1.5:1, which represents a considerable increase over the 1:1 ratio of $Zn(acac)_2$ to $Zn(acHac)_2{}^{2+}$ which constituted the original solution. These results can be explained by postulating the presence of some enol chelate in rapid exchange with the $Zn(acac)_2$. This would increase the area of the methyl peak of $Zn(acac)_2$, as well as shift it toward the enol peak observed at −2.25 ppm for $[Zn(acHac)_2(H_2O)]^{2+}$. In accord with these ideas a decrease in temperature has no effect upon the keto peaks but causes the "acac" methyl and methine peaks to broaden at lower temperatures. The methyl peak remains unresolved until the solution freezes, but the methine peak splits into two peaks with chemical shifts of −5.59 and −5.47 ppm at −70°. The positions of these two peaks agree well with those observed for the methine peaks of $Zn(acac)_2$ and $[Zn(acHac)_2(H_2O)]^{2+}$, respectively. The ratio of keto to "acac" methyl peaks increases with decreasing temperature until at −10° the ratio becomes nearly 1:1 and remains constant at lower temperatures. This indicates an undetectably small amount of enol present at these temperatures, although the line widths of the acac methyl and methine peaks indicate exchange with some species, which must be trace amounts of the enol. Such a fast exchange seems reasonable since it involves only a proton transfer and since the similar exchange between enol and $H_2O$ in $[Zn(acHac)_2(H_2O)]^{2+}$ is fast.

Mixtures of $Zn(acac)_2(H_2O)$ and $[Zn(acHac)_2(H_2O)]^{2+}$ produced results similar to those of the anhydrous compounds discussed above. The major differences are the appearance of an enolic OH peak at −14.8 ppm at −30° and the splitting of the "acac" methyl peak into peaks due to acac and enol at about −60°, although the solution freezes before this resolution is complete. Since both $H_2O$ and acac are present in these solutions, either or both could be contributing to the enolization of the keto form.

The results of the studies of mixtures of acetylacetone and acetylacetonate complexes of Zn(II) show that the $Zn(acac)_2$ complex can act as the necessary base to transform the pure keto form of $Zn(acHac)_2{}^{2+}$ into an equilibrium mixture of keto and enol chelates. Temperature studies of these mixtures, besides revealing the rapid exchange between acac and enol species, show that this equilibrium is temperature dependent with less enol present at lower temperatures. We conclude that a base is necessary to transform $Zn(acHac)_2{}^{2+}$ into an equilibrium mixture of keto and enol isomers.

**Registry No.** $[Zn(acHac)_2(H_2O)](ClO_4)_2$, 38656-87-0; $[Zn(acHac)_2](ClO_4)_2$, 38656-86-9; $Zn(acac)_2$, 14024-63-6.

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(16) D. R. Eaton, *J. Amer. Chem. Soc.*, **87**, 3097 (1965).