$CH_2CONHCH_2COO^-$, and CH_2COO^- (for this structure in the solid state see ref 4), respectively. It is not possible for the CH_2CONH_2 and CH_2COO^- arms to coordinate to a fifth (apical) position.[4] The tetraglycinamide and pentaglycine complexes are remarkably stable and do not decompose completely at pH >5.

The kinetics of protonation of the tetraglycine complex was most extensively studied. A biphasic protonation was observed at 25° in which there was (a) the uptake of one proton ($k = 0.22\ \text{sec}^{-1}$) with an attendent small optical density change at 410 nm ($\sim 10\%$) and (b) the consumption of remaining protons, $k = 0.023\ \text{sec}^{-1}$ (indicator), $0.020\ \text{sec}^{-1}$ (pH-Stat), accompanied by the complete loss of absorption ($k = 0.028\ \text{sec}^{-1}$) at the 410-nm peak. Both protonations could be easily measured by the pH-Stat method at 0° with rate constants of 0.041 and $0.003\ \text{sec}^{-1}$ both at pH 6.7 and 7.3. A final very slow proton change recorded by an indicator in lutidine buffer[6] disappeared in their absence when examined by pH-Stat. Only the first stage was measured by pH-Stat for the other peptides listed, and the rate constant was shown to be pH independent over some 0.5-unit range of pH. The similar rate constants for the first stage at 0° suggest that we are measuring a Ni–N, Ni–O bond rearrangement in the terminal residue in all cases and that, from tetraglycine work, the product is still planar and then undergoes a second discernible protonation at the next peptide residue. The reason for this being so much slower than with triglycine may reside in the long attached grouping hindering inversion.

Conclusion

The acid-independent protonation rate constant for deionized amide and peptide complexes can be rationalized in terms of a mechanism in which an Ni–N bond switch to Ni–O is rate determining. The rate constant for the rearrangement is usually measured directly by k_{H_2O} (k_{obsd}), but when a carboxylate group has to be broken prior to protonation (as with triglycine), a preequilibrium constant is incorporated in k_{H_2O}. The values for k_{H_2O} are not strongly dependent on the structure of the amide or peptide and resemble more closely those for dissociation of nickel(II) complexes with unidentate than bidentate nitrogen ligands.[16]

Acknowledgment.—We are grateful to the National Science Foundation, which supported this work (Grants GP 1963 and GP 8099). We thank the late Mr. Arthur Baase for constructing the stopped-flow apparatus.

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[16] R. G. Wilkins, *Accounts Chem. Res.*, **3**, 408 (1970).

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The Reaction of Some Molybdenum and Tungsten Halides with β-Diketones

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Received February 19, 1971

Dihalobis(β-diketonate) complexes of the group IV metals, in particular $Ti(acac)_2Cl_2$, have been reported in the literature since just after the turn of the century.[1] Although some of the conclusions in the earlier work regarding the geometry[2] and even the polymeric nature[1] of complexes of this type were apparently in error, a number of more recent investigations[3–12] have determined the geometry of a variety of these complexes with some certainty. In all cases studied, including a number of germanium,[4] tin,[3–8] titanium,[9,12] zirconium,[10,12] and hafnium[10–12] compounds, there is overwhelming support for a monomeric cis octahedral structure, based on dipole moment and various spectroscopic results.

Besides the group IV metals, it appears that the only other documented preparation of complexes of the general type $M(diket)_2X_2$ is the preparation of $VCl_2(C_5H_7O_2)_2$ and $VCl_2(C_{10}H_9O_2)_2$ by the reaction of VCl_4 with acetylacetone and benzoylacetone, respectively.[13] In a short paper Larson and Moore reported[14] that $MoCl_4$ reacted with acetylacetone to give a red-purple solid whose elemental analysis approached that of $MoCl_2(acac)_2$. It was postulated that this product was polymeric with a coordination number greater than 6 although no data were given to support this or the proposed formula. This is apparently the only reference to a diketonate complex of either Mo or W in the 4+ oxidation state, although well established complexes in both higher and lower oxidation states are known. The best known of these include $Mo(acac)_3$,[15] $MoO_2(acac)_2$,[16] and $WO_2(acac)$.[17] A number of acetylacetonate complexes of oxymolybdenum species in the 5+ oxidation state have been reported,[18–20] but the existence of some of them has been questioned.[21] This present paper describes a convenient method of preparation of a variety of dihalobis(β-diketonate) complexes of Mo(IV) and W(IV) and discusses the probable structure of these compounds deduced mainly from infrared spectroscopic measurements.

Experimental Section

Preparation of Complexes.—Most of the compounds were synthesized several times. Microanalyses were carried out by Clark Microanalytical Laboratory, Urbana, Ill., and by the Analytical and Information Division, Esso Research and Engineering Co., Linden, N. J. Elemental analyses for all compounds reported in this paper are given in Table I.

Preparation of the Dichlorobis(diketonato)molybdenum(IV) Complexes. Method A. From Molybdenum(V) Chloride.—To a flask containing 5.4 g of $MoCl_5$ (0.02 mol) was slowly added a sufficient quantity of an appropriate solid or liquid β-diketone

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[1] W. Dilthey, *Chem. Ber.*, **37**, 588 (1904).
[2] Y. Kawasaki, T. Tanaka, and R. Okawara, *Spectrochim. Acta, Part A*, **22**, 1571 (1966).
[3] M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 6113 (1964).
[4] J. A. S. Smith and E. J. Wilkins, *ibid.*, *A*, 1749 (1966).
[5] J. W. Faller and A. Davidson, *Inorg. Chem.*, **6**, 182 (1967).
[6] I. Douek, M. J. Frazer, Z. Goffer, M. Goldstein, B. Rimmber, and H. Willis, *Spectrochim. Acta, Part A*, **23**, 373 (1967).
[7] W. H. Nelson, *Inorg. Chem.*, **6**, 1509 (1967).
[8] V. Doron and C. Fischer, *ibid.*, **6**, 1917 (1967).
[9] R. C. Fay and R. N. Lowry, *ibid.*, **6**, 1512 (1967).
[10] T. J. Pinnavaia and R. C. Fay, *ibid.*, **7**, 502 (1968).
[11] R. C. Fay and T. J. Pinnavaia, *ibid.*, **7**, 508 (1968).
[12] N. Serpone and R. C. Fay, *ibid.*, **8**, 2379 (1969).
[13] H. Funk, G. Mohaupt, and A. Paul, *Z. Anorg. Allg. Chem.*, **302**, 199 (1959).
[14] M. L. Larson and F. W. Moore, *Inorg. Chem.*, **3**, 285 (1964).
[15] M. L. Larson and F. W. Moore, *ibid.*, **1**, 856 (1962).
[16] G. T. Morgan and R. A. S. Castell, *J. Chem. Soc.*, 3252 (1928).
[17] A. Nikolovski, *Croat. Chem. Acta*, **40**, 143 (1968).
[18] I. Bernal, *Chem. Ind. (London)*, 1343 (1966).
[19] A. Rosenheim and C. Nernst, *Z. Anorg. Allg. Chem.*, **214**, 216 (1933).
[20] P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **21**, 883 (1964).
[21] H. Gehrlce and J. Veal, *Inorg. Chim. Acta*, **3**, 623 (1969).

TABLE I

ANALYTICAL DATA FOR $M(diket)_2Cl_2$ AND RELATED COMPOUNDS

Complex	Diketone	% found C	% found H	% found Cl	Mol wt found	% calcd C	% calcd H	% calcd Cl	Mol wt calcd
$Mo(acac)_2Cl_2$	Acetylacetone	32.47	3.80	19.80		32.89	3.86	19.42	
$Mo(hpd)_2Cl_2$	3,5-Heptanedione	40.00	5.18		384[a]	40.01	5.26		421
$Mo(nnd)_2Cl_2$	4,6-Nonanedione	43.57	6.00			45.42	6.33		
$Mo(mhpd)_2Cl_2$	6-Methyl-2,4-heptanedione	42.28	5.50		455[a]	42.91	5.85		449
$Mo(dibm)_2Cl_2$	Diisobutyrylmethane	43.97	5.80		494[a] 485[b]	45.40	6.33		477
$Mo(dpm)_2Cl_2$	Dipivaloylmethane	49.29	6.90	14.16	491[a] 525[b]	49.54	7.18	13.29	533
$Mo(3\text{-}Cl(acac))_2Cl_2$	3-Chloro-2,4-pentanedione	27.11	2.65	32.28		27.35	2.75	32.12	
$Mo(3\text{-}C_6H_5acac)_2Cl_2$	3-Phenyl-2,4-pentanedione	50.68	4.37	14.26		50.95	4.30	13.73	
$Mo(bzac)_2Cl_2$	Benzoylacetone	47.98	3.68			49.08	2.70		
$Mo(dbzm)_2Cl_2$	Dibenzoylmethane	57.60	3.79	11.61		57.07	3.51	11.23	
$Mo(ttfa)_2Cl_2$	Thenoyltrifluoroacetone	31.16	1.27	11.87		31.55	1.32	11.64	
$Mo(achx)_2Cl_2$	2-Acetylcyclohexanone	42.61	4.58	16.03		42.97	5.40	15.85	
$W(acac)_2Cl_2$		26.80	3.36	14.64		26.55	3.12	15.61	
$W(mhpd)_2Cl_2$		35.61	5.04	11.50		35.82	4.77	13.21	
$W(dbzm)_2Cl_2$		51.04	3.43	9.53		50.03	3.08	9.81	
$W(acac)_2Br_2$		22.73	2.65	28.09[c]		22.20	2.60	29.45[c]	

[a] Freezing point depression in benzene. [b] Vapor pressure depression in methylene chloride at 0°. [c] Per cent bromine.

so that the molar ratio of β-diketone to $MoCl_5$ was at least 3:1. The resulting mixture was then heated to 120° with stirring for a few minutes until evolution of HCl ceased. After cooling, the resulting reaction mixture was extracted several times with hot heptane leaving the solid product. The more insoluble complexes, such as those derived from acetylacetone, dibenzoylmethane, or 3-chloroacetylacetone were purified by repeatedly washing with hot CCl_4 followed by pentane and were then dried by sucking nitrogen through the solid complex on a filter. The more soluble complexes were purified by recrystallization from a minimum volume of CCl_4. Yields were usually greater than 80%.

Method B. From Molybdenum(IV) Chloride.—To a flask containing 4.8 g of $MoCl_4$ (0.02 mol) was added a large excess of the β-diketone. The resulting mixture was heated with stirring at 125° until it was certain that all the dark $MoCl_4$ had reacted. The reaction time depended on the β-diketone used. For the more reactive β-diketones, such as acetylacetone, about 2–3 hr sufficed, whereas less reactive materials such as dipivaloylmethane required heating for 12 hr or more. After cooling the reaction mixture, the excess β-diketone and other organic materials were washed out with pentane leaving the solid molybdenum dichlorobis(diketonate) complex. Purification was carried out as described above.

Preparation of the Dihalobis(diketonato)tungsten(IV) Complexes.—These complexes were prepared from WCl_5[22] or WBr_5 and the appropriate β-diketones in a manner exactly analogous to the preparation of the molybdenum derivatives as described in method A above.

Results and Discussion

The reaction of metal halides with free β-diketones according to the general equilibrium

$$MX_a + bH(diket) \rightleftharpoons MX_{a-b}(diket)_b + bHCl$$

is one of the most useful methods of preparing mixed halodiketonate complexes.

Molybdenum pentachloride reacts vigorously with neat acetylacetone at room temperature with the evolution of HCl to give a dark red-brown solid material with the composition $Mo(acac)_2Cl_2$. This reaction appears to be quite general for most β-diketones, including those with straight or branched alkyl groups, aryl groups, and some halides as substituents, although certain fluorinated compounds such as hexafluoroacetylacetone do not react in this manner to give isolable products. In all cases, reduction of the metal occurs and the product has the general formula $Mo(diket)_2Cl_2$. Tungsten pentachloride and pentabromide undergo similar reactions but at somewhat higher temperatures than the molybdenum analogs.

The reaction of $MoCl_5$ with β-diketones therefore differs markedly from its reaction with carboxylic acids where one simply replaces two chlorine ligands to obtain complexes of the type $Mo(RCOO)_2Cl_3$ without reduction of the molybdenum.[23]

The fact that the $MoCl_5$ and WCl_5 react so readily to give good yields of reduced dichlorobis(diketonate) complexes suggested that these complexes might be synthesized directly from the metal tetrahalides. Indeed, on prolonged heating of $MoCl_4$ with acetylacetone or any of several other β-diketones, products are formed identical with those obtained from $MoCl_5$ and the diketones.

The reaction of acetylacetone with $MoCl_4$ is straightforward but with $MoCl_5$ the acetylacetone must also function as a reducing agent, reducing the molybdenum to Mo(IV). This reduction is not completely unexpected since it is known that even relatively inert materials, including hydrocarbons such as benzene, reduce $MoCl_5$ to $MoCl_4$.[14] Acetylacetone is known to function as a reducing agent as is shown by its reduction of V_2O_5 to form $VO(acac)_2$.[24] The products of the oxidation of the acetylacetone are not known. Because of the high reactivity of the γ position to halogen substitution it was thought that 3-chloroacetylacetone would be a major product. Analysis of the organic reaction products by gas-phase chromatography showed this supposition to be incorrect. At least seven different products could be resolved but none of them were 3-chloroacetylacetone.

It is of interest to note that $NbCl_5$ and $TaCl_5$ also do not react with β-diketones to give the simple substitution products. Funk[25] has reported that these pentahalides react vigorously with the diketones to give impure reaction products due to decomposition of the diketones. Apparently at least one metal pentahalide, namely, antimony pentachloride does react with diketones to give compounds of the type $SbCl_4(diket)$[26] without decomposition.

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(22) T. M. Brown and E. L. McCann III, *Inorg. Chem.*, **7**, 1227 (1968).

(23) M. L. Larson, *J. Amer. Chem. Soc.*, **82**, 1223 (1960).

(24) R. A. Rowe and M. M. Jones, *Inorg. Syn.*, **5**, 114 (1956).

(25) H. Funk, *Chem. Ber.*, **67**, 1801 (1934).

(26) W. Dilthey, *J. Prakt. Chem.*, **111**, 147 (1925).

The insolubility of $Mo(acac)_2Cl_2$ in even fairly polar organic solvents suggested that a polymeric structure for these complexes may be possible even though a monomeric structure seemed most likely. Because of its low solubility, molecular weight studies could not be carried out on $Mo(acac)_2Cl_2$; however, determinations were made on some other representative compounds including $Mo(hpd)_2Cl_2$, $Mo(dpm)_2Cl_2$, $Mo(nhpd)_2Cl_2$, and $Mo(dibm)_2Cl_2$. With the exception of $Mo(hpd)_2Cl_2$, the values obtained by both the freezing point depression and the vapor pressure depression methods were in excellent agreement with the calculated values for monomeric species.

The reason for the insolubility of $Mo(acac)_2Cl_2$ is not known but there is a graduated increase in the solubility of the complex with the size and number of organic substituents on the diketonate ligands. Since all the complexes whose molecular weights were measured are monomeric, including $Mo(hpd)_2Cl_2$ whose steric interactions are only slightly more severe than $Mo(acac)_2Cl_2$, it seems most likely that all the complexes in this series, including $Mo(acac)_2Cl_2$, are also monomeric and that the postulate of Larson and Moore[14] regarding the polymeric nature of $Mo(acac)_2Cl_2$ may be incorrect. The low solubility of $Mo(acac)_2Cl_2$ does not seem to be irregular and there is no apparent reason why the coordination number of Mo should be greater than 6 in this complex.

At the present time, it is not possible to say whether these complexes exist as the cis or trans isomers. Because of their paramagnetic nature nmr measurements are precluded and infrared data, although perhaps suggesting a cis configuration, are inconclusive.

The infrared spectrum of $Mo(acac)_2Cl_2$ together with tentative assignments is given in Table II. The identification of the acetylacetonate vibrations were made by comparison with the spectra of $Mo(acac)_3$,[15] $Mo_2O_3(acac)_4$,[21] $MoO_2(acac)_2$,[27] and several $Ti(acac)_2X_2$ complexes.[28] The assignments for the acetylacetonate ligands are based on the normal-coordinate analysis of metal acetylacetonates by Nakamoto[29] modified slightly by later work with the deuterated ligand.[30] The spectrum is consistent only with chelated acetylacetonate ligands and the absence of strong carbonyl bands at frequencies higher than 1600 cm^{-1} in the spectra of the other $M(diket)_2Cl_2$ complexes shows that the diketonate ligands in these complexes are also chelated in the normal fashion. The two fairly intense bands which are seen in the spectrum of $Mo(acac)_2Cl_2$ at 342 and 312 cm^{-1} have tentatively been assigned as Mo–Cl stretching vibrations. This assignment seems to be quite reasonable since bands are observed in this region for several other $Mo(diket)_2Cl_2$ complexes and Mo–Cl stretching vibrations are known to occur in the 300–400-cm^{-1} region.[31,32] Further, examination of a number of molybdenum acetylacetonate complexes reveals that no strong ligand vibrations are seen in this spectral region and that Mo–O stretching vibrations are usually seen at much higher frequencies. Only one Mo–Cl stretching band should be seen in the spectrum of the more symmetrical trans isomer; however, this evidence is much too speculative to rule out a trans structure.

TABLE II

INFRARED SPECTRA OF $Mo(acac)_2Cl_2$

ν,[a] cm^{-1}	Assignment	ν,[a] cm^{-1}	Assignment
1525 vs	$C\overset{\cdots}{-}O$ str + $C\overset{\cdots}{-}C$ str	818 s	C–H out-of-plane def
1410 m	CH_3 degen def	676 s	Ring def + Mo–O str
1362 m	CH_3 sym def	595 m	Mo–O str
1340 m	$C\overset{\cdots}{-}O$ str	542 vs	Out-of-plane def
1286 s	$C\overset{\cdots}{-}C$ str	469 s	$C–CH_3$ def + Mo–O str
1019 m	CH_3 rock	420 m	In-plane def
938 w	$C–CH_3$ str + $C\overset{\cdots}{-}O$ str	342 s	Mo–Cl str
927 m		312 m	Mo–Cl str

[a] Key: s, strong; m, medium; w, weak; v, very.

Acknowledgments.—I wish to thank Dr. W. R. Kroll for many helpful discussions, Dr. G. B. McVicker and Mrs. S. Pagnucco for obtaining the molecular weight data, and especially Mr. J. W. Swirczewski for his excellent experimental assistance.

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[27] B. Soptrajanov, A. N. Kolovski, and I. Petrov, *Spectrochim. Acta, Part A*, **24**, 1617 (1968).

[28] R. C. Fay, N. Serpone, and R. N. Lowry, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, Paper L-071.

[29] K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

[30] G. T. Benke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

[31] R. J. Clark, *Halogen Chem.*, **3**, 85 (1967).

[32] R. F. W. Bader and K. P. Huang, *J. Chem. Phys.*, **43**, 3760 (1965).

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Cobalt-59 Nuclear Magnetic Resonance Study of Acid Dissociation Equilibria in Aquopentaamminecobalt(III) Perchlorate and *cis*- and *trans*-Aquoamminebis(ethylenediamine)cobalt(III) Bromide

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Received February 1, 1971

Nuclear magnetic resonance (nmr) of metal ions such as Al(III),[1,2] Ga(III),[3] and Cu(I)[4] is quite useful in studying kinetics and equilibrium of metal complexes in solution. In the present study ^{59}Co line widths and chemical shifts are measured to investigate the acid dissociation equilibria and kinetics of proton exchange in concentrated (≥ 0.20 *M*) aqueous solutions of $[Co(NH_3)_5H_2O](ClO_4)_3$ and *cis*- and *trans*-$[Co(en)_2NH_3H_2O]Br_3$.

Experimental Section

$[Co(NH_3)_5H_2O](ClO_4)_3$ and *cis*- and *trans*-$[Co(en)_2NH_3H_2O]Br_3$ were prepared by the typical procedures given in the literature.[5,6]

Nmr measurements were made at 25.0° with the use of a JEOL LNM-WB-20 spectrometer operating at 13.557 MHz. Some measurements were carried out on a Varian VF-16 spectrometer at several frequencies. Chemical shifts were measured in aqueous solution containing a trace amount of $Co(en)_3^{3+}$ ion as an internal standard. Line widths were obtained as the

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[1] H. Haraguchi and S. Fujiwara, *J. Phys. Chem.*, **73**, 3467 (1969).

[2] J. W. Akitt, N. N. Greenwood, and G. D. Lester, *J. Chem. Soc. A*, 803 (1969).

[3] A. Fratiello, R. E. Lee, and R. E. Schuster, *Inorg. Chem.*, **9**, 82 (1970).

[4] T. Yamamoto, H. Haraguchi, and S. Fujiwara, *J. Phys. Chem.*, **74**, 4369 (1970).

[5] F. Ephraim, *Ber.*, **56**, 1536 (1923).

[6] H. F. Holtzclaw, Jr., *Inorg. Syn.*, **8**, 200 (1966).