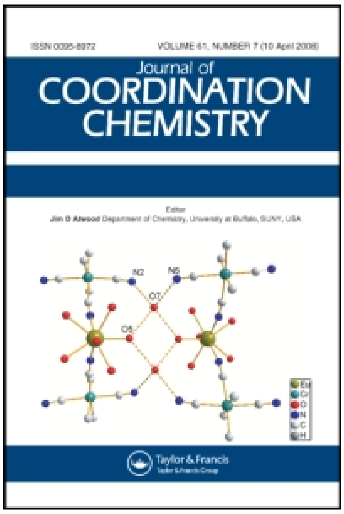

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# DI-, TRI- AND POLY-NUCLEAR TRANSITION METAL COMPLEXES OF 3,4-DIACETYL-2,5-HEXANEDIONE

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# DI-, TRI- AND POLY-NUCLEAR TRANSITION METAL COMPLEXES OF 3,4-DIACETYL-2,5-HEXANEDIONE

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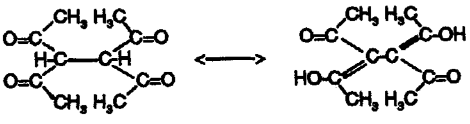
3,4-Diacetyl-2,5-hexanedione (tetraacetylethane) is a tetradentate dibasic ligand and constitutes two acetylacetone molecules linked together through the central carbon. The ligand is thus capable of coordinating two metal cations. Its reaction with Cu(II), Ni(II), Co(II), Fe(III) and Cr(III) yielded the corresponding complexes, [(M(L-2H)] for Cu(II) and Ni(II), basic Co(III) complex [Co(L-2H)(OH)] and [M(2L-3H) for Fe(III) and Cr(III). These complexes were characterized by their IR, visible and mass spectra and by magnetic measurements. All complexes have octahedral configurations. The mass spectra of the complexes indicated peaks with m/e values higher than the parent peaks, where Ni(II), and Co(III) complexes are dimers and the Cu(II) complex is trimeric. This coupled with the insolubility of the complexes in all common solvents indicates the polymeric nature of the products.

KEYWORDS: polydentate, transition metal complex, 3,4-diacetyl-2,5-hexanedione

## INTRODUCTION

Acetylacetonate complexes of metals are known and their structures differ considerably. They are either monomeric or polymeric species and the polymeric complexes differ in their structures according to their type of polymerization.[1-4]

Tetraacetylethane (3,4-diacetyl-2,5-hexanedione) was prepared by the reaction of sodium acetylacetonate and iodine in dry either.[5] This ligand constitutes two acetyacetone molecules linked together through their central carbon atoms (Structure 1). Thus, this ligand is capable of coordinating two metal cations. The reaction of the ligand with some transition metal cations are presented and the structures of the formed complexes discussed.



**Structure 1**

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## EXPERIMENTAL

Acetylacetone was a BDH product and freshly distilled before use. Sodium and lithium hydroxides, metal salts and organic solvents were all reagent grade. The acetates of Cu(II), Ni(II) and Co(II), and the chlorides of Fe(III) and Cr(III) were used.

### *Preparation of the Ligand*

The ligand was prepared by the procedure of Charles[5] and its m.p. is 192°C.

### *Preparation of the Metal Complexes*

Cu(II) and Ni(II) were prepared by addition of a hot methanolic solution of LiOH to a hot methanolic solution of the ligand, molar ratio 2:1, where a yellow coloured solution was produced. A methanolic solution of the metal acetate was then added gradually to the previous solution while both were hot. The solution was stirred continuously during addition of the reactants and precipitation usually occurred. The products were obtained by filtration and washed several times with small amounts of methanol. The molar ratio of the ligand:metal was 2:1 and 3:1 for divalent and trivalent metal cations, respectively.

The Co(III) complex was prepared as a green precipitate using the procedure above, however, floating traces of a pink product appeared. In other preparations, the solutions were added after cooling in ice, a pink precipitate was obtained and filtered immediately. From the filtrate a green precipitate, the basic Co(III) complex, was obtained either by heating or if left overnight. The pink precipitate turned slowly to either brownish red violet or brownish green solid.

In the preparations of Fe(III) and Cr(III) complexes, LiOH was not used. Instead anhydrous sodium acetate and urea were used, respectively, similar to the preparation of acetylacetonato complexes.[6,7] Also, the chlorides of Fe(III) and Cr(III) were used instead of the metal acetates in the previous preparations.

The products were insoluble in all common solvents. Analytical data for the prepared complexes together with their uncorrected melting points are shown in Table 1.

IR spectra were recorded on a Perkin-Elmer 598 spectrometer using KBr discs. Electronic spectra of the solids were recorded on a Beckman Acta MIV spectrophotometer provided with a diffuse reflectance attachment. Magnetic susceptibilities of the solid complexes were determined by the Gouy method. Diamagnetic corrections were calculated from Pascal's constants. Mass specta of the complexes were recorded on Fiuuijan MAT 8200 spectrometer. Samples were introduced directly in the probe. The ionizing beam potential was 70 eV.

Microanalyses of carbon and hydrogen were carried out at the Microanalytical Centre, Giza, Egypt. Analyses of the metals in the complexes were achieved by dissolving the solid complex in hot concentrated HCl, then diluting with water and filtering to remove the precipitated ligand. Aqueous solutions of the metals were then titrated with EDTA. Cobalt(III) complexes were dissolved in concentrated $HNO_3$.

**Table 1** Analytical data, magnetic moments and electronic spectra of metal complexes

| Complex | Mol. formula | Colour | yield % | m.p. (°C) | Analyses: Found/(Calc.) %C | %H | %M | Magnetic moment (B.M.) | Electronic spectra (cm$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|
| [Cu(L-2H)] | $C_{10}H_{12}O_4Cu$ | light green | 90 | >220 | 46.0<br>(46.2) | 4.2<br>(4.7) | 24.4<br>(24.5) | 1.81 | $^2B_{1g} \rightarrow ^2A_{1g}$ | 15300 |
| [Ni(L-2H)]·2H$_2$O | $C_{10}H_{16}O_6Ni$ | bluish green | 88 | deeper colour at 180 | 41.0<br>(41.3) | 5.3<br>(5.5) | 20.1<br>(20.2) | 2.67 | $^3A_{2g} \rightarrow ^3T_{1g}$<br>$^3A_{2g} \rightarrow ^3T_{1g}$<br>$^3A_{2g} \rightarrow ^3T_{1g}$ | 8850<br>15400<br>24700 |
| [Co(L-2H)(OH)]·2H$_2$O | $C_{10}H_{17}O_7Co$(A) | brownish-red violet | 45 | >220 | 39.0<br>(39.0) | 5.6<br>(5.6) | 18.5<br>(19.0) | — | — | |
| [Co(L-2H)(OH)]·H$_2$O | $C_{10}H_{15}O_6Co$(B) | Green | 41 | changes to brown at 210 | 40.9<br>(41.4) | 5.1<br>(5.2) | 19.8<br>(20.3) | Diamag. | $^1A_{1g} \rightarrow ^3T_{1g}$<br>$^1A_{1g} \rightarrow ^1T_{1g}$ | 8500<br>15900 17100 |
| Fe(2L-3H) | $C_{20}H_{25}O_8Fe$ | reddish orange | 73 | >220 | 53.4<br>(53.3) | 5.1<br>(5.6) | 12.2<br>(12.4) | 5.76 | charge transfer band tailing into the visible region | |
| [Cr(2L-3H)]·4H$_2$O | $C_{20}H_{33}O_{12}Cr$ | reddish grey | 39 | lighter colour at 200 | 45.7<br>(46.4) | 5.7<br>(6.4) | 10.0<br>(10.1) | 3.80 | $^4A_{2g} \rightarrow ^4T_{2g}$<br>$^4A_{2g} \rightarrow ^4T_{1g}$ | 17500<br>24700 |

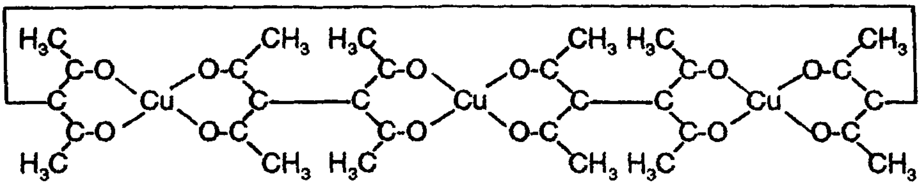
## RESULTS AND DISCUSSION

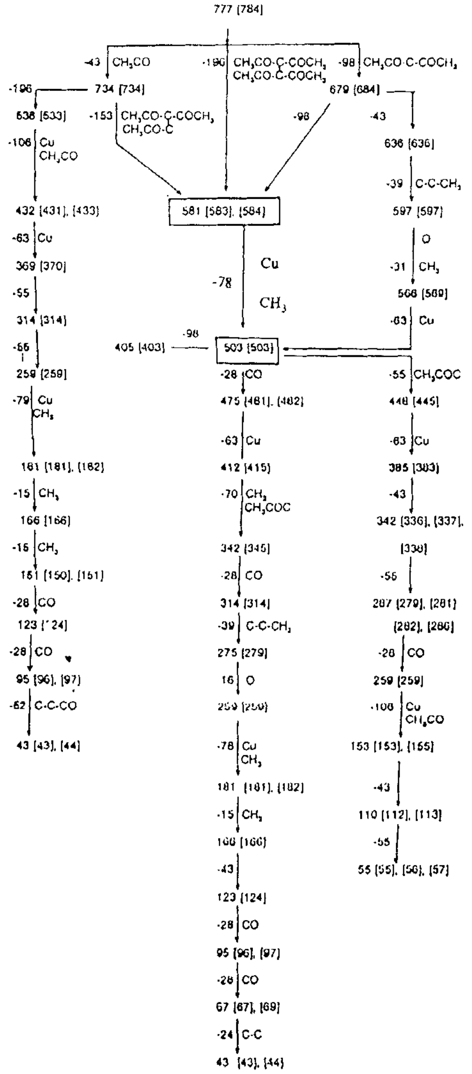
Tetraacetylethane is a tetradentate dibasic ligand and its reaction with transition metal cations Cu(II), Ni(II), Co(II), Fe(III), Cr(III) yielded the corresponding metal complexes except Co(II) where basic Co(III) isomeric complexes were obtained. Analytical data, Table 1, point to a simple formula involving one molecule of ligand per each atom in the case of Cu(II), Ni(II) and Co(III). The latter complex is a basic complex and contains an OH group per each molecule. Complexes of Cr(III) and Fe(III) involve two molecules of the ligand per each metal atom. From the absence of any counter-ion, charge balance and coordination number it could be concluded that one molecule of the ligand is twice deprotonated in the case of divalent cations and Co(III) complexes or two molecules of the ligand trice deprotonated in the case of Fe(III) and Cr(III). LiOH was used in the reactions of divalent metals with the ligand as a deprotonating agent. The insolubility of the products in all common solvents suggests their polymeric nature.

Cobalt(II) acetate yielded two Co(III) basic products. The green product obtained from the filtrate is considered to be the *trans*-form by analogy of other known *trans*-cobalt(III) complexes.[8] The pink precipitate, most likely a cobalt(II) product, undergoes oxidation and changes its colour either to a brownish red violet or a brownish green solid. The chemical analyses of the green and the brownish red violet products showed that they have the same molecular formula but differ in the number of lattice water molecules.

The Cu(II) complex is a paramagnetic light green polymer, as indicated by its insolubility in all common solvents. Its visible spectrum showed a single unsymmetrical absorption band at 15300 $cm^{-1}$, however, as already noted, the $d^9$ ion is characterized by large distortions from octahedral symmetry and the band is unsymmetrical as a result of a number of transitions which are by no means assigned unambiguously. The magnetic moment of the Cu(II) complex is 1.81 B.M. In general, moments of magnetically dilute complexes are in the range 1.9–2.2 B.M., with compounds whose geometries approach octahedral having moments at the lower end, and those with geometries approaching tetrahedral having moments at the higher end. As a result, each copper atom achieves octahedral coordination through additional oxygen atoms in neighbouring molecules. The molecular weight was determined from the highest mass peak in its mass spectrum. The Cu(II) complex is a trimer, which gives a parent ion at m/e 784 a.m.u. (calculated value 777 a.m.u.). In the mass spectrum, the trimer of the Cu(II) complex may break down to a mixture of neutral and positively charged fragments as shown in Scheme 1. Further fragmentation can then occur, so that the spectrum which is recorded contains many ions, depending on a number of factors, including their stabilities and stabilities of their precursors. The mass and visible spectra and the magnetic moment agree with a trimeric structure, Structure 2. The modeling structure of this trimer shows that only oxygen is tetrahedrally bridged to three Cu(II) cations and one carbon atom, similar to that observed in metal alkoxides.[9]

The Ni(II) complex is a paramagnetic blue green polymer, insoluble in all common solvents, and also has octahedral symmetry. The extra two water molecules in its molecular formula besides the four oxygen atoms of two neighbouring molecules provide the octahedral configuration. Its visible spectrum showed three absorption peaks at 8850, 15400 and 24700 $cm^{-1}$ corresponding to the three

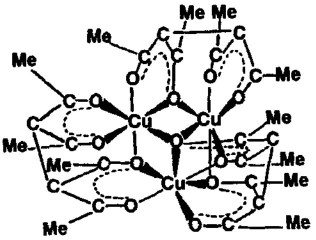




**Scheme 1**

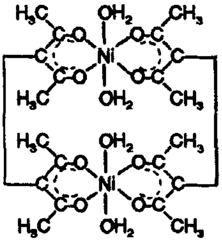
* Calc/[Found].

N.B.: Differences between calculated and found values are due to abstraction or addition of free H radicals, examples are given in Scheme 2.



**Structure 2** Trimeric Cu(II) complex.

expected transitions of Ni(II) in octahedral symmetry. Its magnetic moment, 2.67 B.M., supports this conclusion. A deeper colour is developed at 180°C, which may be due to loss of the two water molecules which are coordinated to each nickel atom. The Ni(II) complex is a dimer, where the highest mass peak in its mass spectrum is observed at m/e 505 a.m.u. (calculated value 510 a.m.u. after subtracting two water molecules). The dimer may then break down into a mixture of neutral and positively charged fragments as shown in Scheme 2. The data agree with the proposed structure of the Ni(II) complex, Structure 3.

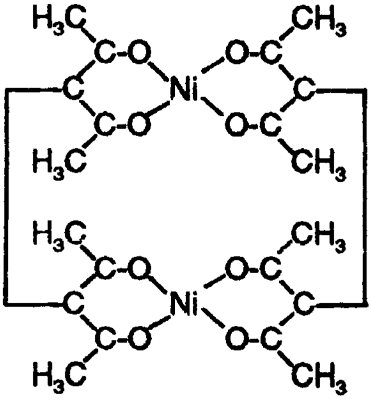


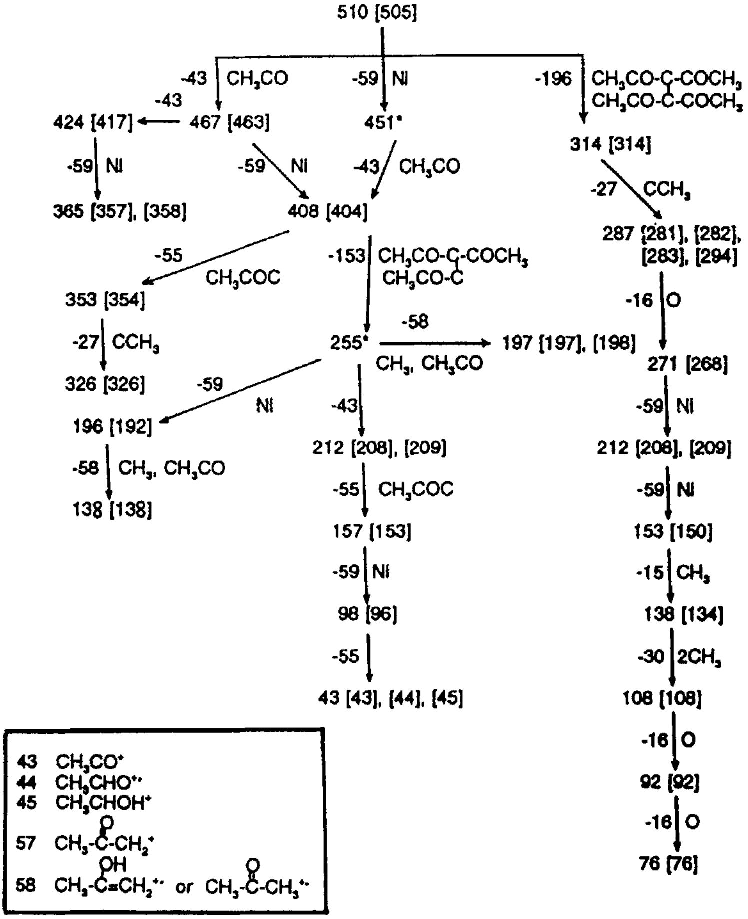
**Structure 3** The Dimeric Ni(II) complex.

The green basic Co(III) complex was studied in more detail. Its visible spectrum showed three transitions at 8500, 15900 and 17100 $cm^{-1}$. The first peak was assigned to the spin forbidden $^1A_{1g} \rightarrow {}^3T_{1g}$ transition, while the latter two transitions were both assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The splitting of the latter transition indicates that this compound has a *trans* structure. The $^1T_{1g}$ state splits significantly more for *trans* isomers, than for *cis* complexes.[10,11] This complex was also diamagnetic. This result coupled with the observed visible transitions of the complex indicates a low-spin octahedral arrangement of the ligands. Structure 4 shows the suggested *trans*-octahedral structure.

The mass spectrum of the green Co(III) complex indicates that it is a dimer, which gives a parent ion at m/e 505 a.m.u. (calculated value 510 a.m.u. after subtracting the water molecules and the coordinated OH groups). The dimer may then break down into neutral and positively charged fragments as shown in Scheme 3.

Both Fe(III) and Cr(III) gave complexes of the same molecular formula [M(2L-3H)] and the latter complex has four lattice water molecules. The visible spectrum of the Fe(III) cation was obscured by a charge transfer band tailing into the visible





Scheme 2

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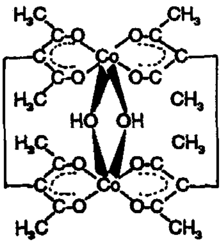
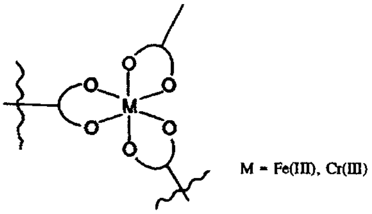
* There are no peaks corresponding to these entitles.



Structure 4 *trans*-octahedral basic Co(III) complex.

region. Cr(III) shows two peaks in its visible spectrum at 17500 and 24700 cm$^{-1}$ due to $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions. The magnetic moments of these complexes are 5.76 and 3.80 B.M., respectively. These results indicate octahedral arrangements of the ligands in these complexes. Structure 5 shows the suggested structure of these complexes.



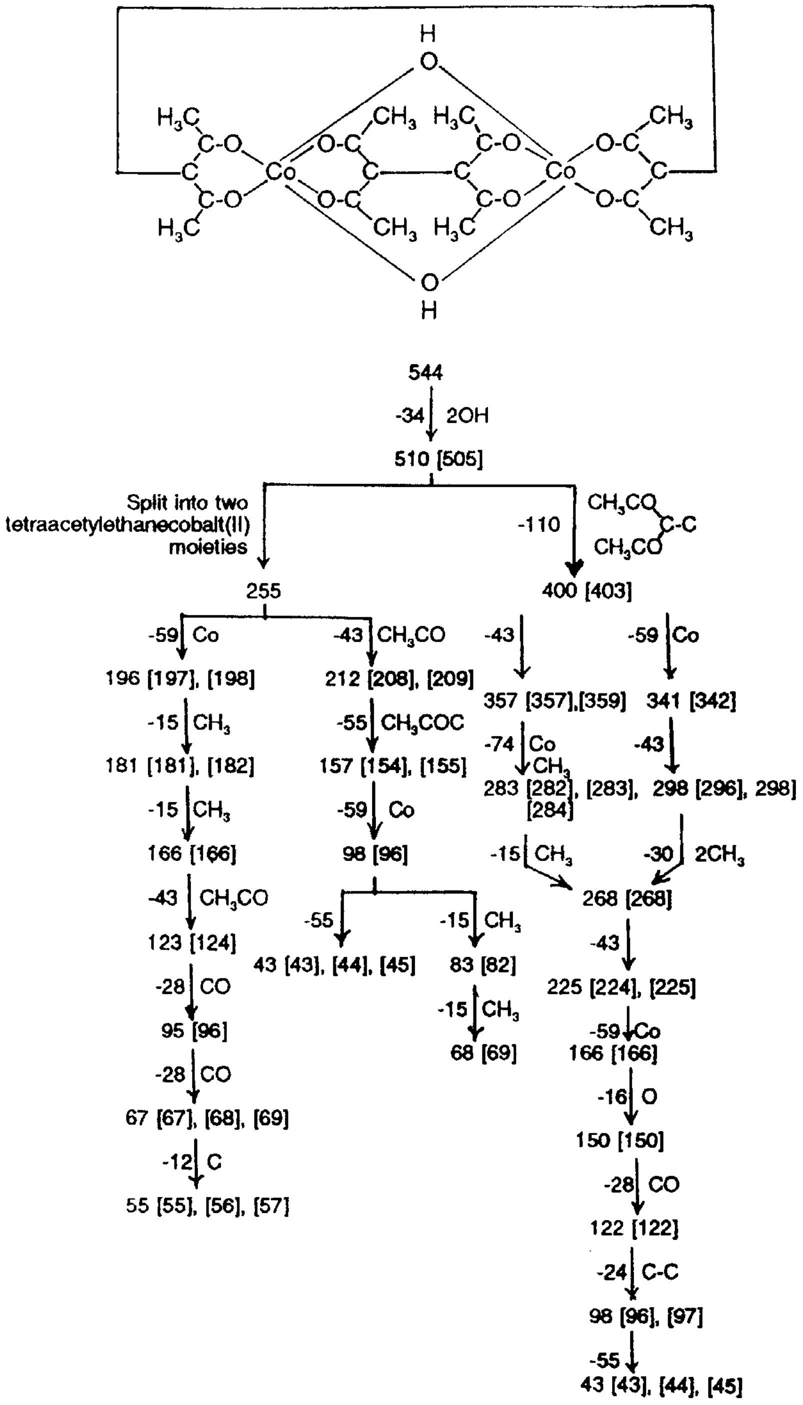
Structure 5 Octahedral Fe(III) or Cr(III) complexes.

The mass spectra of the Fe(III) and Cr(III) complexes show peaks of m/e higher than those of the parent ions at 784 and 431 a.m.u. for the Fe(III) and Cr(III) complexes, respectively, besides various fragmentations of the complexes and ligand molecules. The observation of peaks of higher m/e values indicates the polymeric nature of the two complexes which is also shown by their insolubility in all common solvents.

All of the complexes show slightly low magnetic moments which may be associated with weak antiferromagnetic coupling between metal centers in the dimeric, trimeric or polymeric structures.

The IR spectra of these complexes, have been recorded to confirm their structures. The vibrational frequencies and their tentative assignments are listed in Table 2. The assignments were aided by comparison with the vibrational frequencies of the free ligand, tetraacetylethane, $M(acac)_2 \cdot 2H_2O$ (M=Ni(II), Cu(II); acac =acetylacetonate) complexes[12] and by theoretical calculations on $M(acac)_2$ (M= Pd(II), Cu(II), Ni(II), Co(II), Zn(II)) and $M(acac)_3$ (M=Co(III), Cr(III), Fe(III), Al(III)).[13] The IR spectra of these complexes are similar to those of the $M(acac)_2 \cdot 2H_2O$.

The complexes are expected to possess $D_{2h}$, $D_{3h}$ or $C_s$ symmetries. Therefore, a total of 3N-6 normal modes are predicted for these complexes; most of them are IR inactive due to the highly symmetric nature of the complexes.


H
O
H₃C
C-O
C
C-O
H₃C
Co
O-C
CH₃
C
O-C
CH₃
H₃C
C-O
C
C-O
H₃C
Co
O-C
CH₃
C
O-C
CH₃
O
H
544
-34 2OH
510 [505]
Split into two tetraacetylethanecobalt(II) moieties
-110
CH₃CO C-C CH₃CO
255
400 [403]
-59 Co
-43 CH₃CO
-43
-59 Co
196 [197], [198]
212 [208], [209]
357 [357],[359]
341 [342]
-15 CH₃
-55 CH₃COC
-74 Co CH₃
-43
181 [181], [182]
157 [154], [155]
283 [282], [283], [284]
298 [296], 298]
-15 CH₃
-59 Co
166 [166]
98 [96]
-15 CH₃
-30 2CH₃
-43 CH₃CO
-55
-15 CH₃
268 [268]
123 [124]
43 [43], [44], [45]
83 [82]
-43
-28 CO
-15 CH₃
225 [224], [225]
95 [96]
68 [69]
-59 Co
166 [166]
-28 CO
-16 O
67 [67], [68], [69]
150 [150]
-12 C
-28 CO
55 [55], [56], [57]
122 [122]
-24 C-C
98 [96], [97]
-55
43 [43], [44], [45]

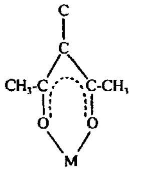
Scheme 3

**Table 2** Infrared frequencies and assignments of the ligand and its metal complexes*

| $H_2L$ | [Cu(L-2H)] | [Ni(L-2H)·$2H_2O$] | [Co(L-2H)(OH)·$2H_2O$] | [Co(L-2H)(OH)·$H_2O$] | [Fe(2L-3H)] | [Cr(2L-3H)·$4H_2O$] | Assignments |
|---|---|---|---|---|---|---|---|
| | | 3360 vs,b | 3400 vs,b | 3410 s,b | | 3410 s,b | $\nu_{as}(H_2O)$ + ν(OH) |
| | | | | 3310 s,b | | 3370 s,b | |
| | | | | 3168 s,b | | 3310 s,b | |
| | | | | | | 3168 s,b | |
| 2990 vw | 2970 vw,b | 2900 vw,b | 2980 w | 2980 vw | 2990 vw | 2935 w | |
| 2950 sh | 2950 w | 2950 vw | 2920 vw | 2900 sh | 2950 vw | 2890 w | $\nu(CH_3)$ |
| 2910 vw | 2910 sh | 2910 vw | | 2890 w | 2900 vw | | |
| | | 1650 sh | 1610 sh | 1630 sh | | 1640 sh | $\delta(H_2O)$ + δ(OH) |
| | | | | | | 1600 sh | |
| 2560 m | | | | | | | ν(H-bonded OH) |
| 1585 vs,b | 1555 sh | 1560 vs,b | 1550 vs,b | 1550 vs,b | 1545 vs,b | 1530 vs,b | ν(C-O) + ν(C-C) |
| | 1540 vs | | | | | | |
| | | | | 1430 sh | | 1430 vs,b | ν(C-O), δ(C-C-C) |
| 1405 vs,b | 1405 vs | 1400 vs,b | 1405 vs,b | 1400 vs,b | 1405 vs,b | 1405 vs,b | $\delta_d(CH_3)$ |
| 1360 vs,b | 1355 vs | 1350 vs,b | 1350 vs | 1368 s | 1350 s | 1340 sh | $\delta_s(CH_3)$ |
| 1310 sh | 1330 vs | 1310 sh | 1330 vs | 1335 s | 1320 vs,b | 1315 vs,b | |
| 1245 s | 1260 m | 1240 s | 1260 m | 1238 s | 1255 s | 1250 vs,b | ν(C-C) + $\nu(C\text{-}CH_3)$ |
| | | | | | | 1150 w,b | |
| 1010 s | 1005 m | 1000 m | 1015 m | 1000 m | 1000 m | 1000 s | $\rho_r(CH_3)$ |
| 990 s | | | | | | | δ(H-bonded OH) |
| 930 w | 940 m | 935 w | 945 m | 930 m | 940 m | 935 s | δ(C-C-C) |
| 910 w | 915 m | 905 m | 910 sh | 900 m | 910 m | 908 m | $\nu(C\text{-}CH_3)$ + ν(C-O) |
| | | | | | | 895 m | |
| 675 w | 690 w | 675 w | 700 w | 680 w,b | 690 vw | 680 w | $\delta(C\text{-}CH_3)$ + ν(M-O) |
| 670 w | | 670 w | 670 vw | | 665 w | | + ring def. |
| | | | 645 vw | | | | |
| 540 w | 500 w | 500 w | 515 vw | | | | π |
| | 460 m | 440 w | 470 w | 490 w | 445 w | 480 w | ν(M-O) |
| 480 w | | 405 w | 425 w | 450 w | | 450 w | π |

* s = strong, vs = very strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad.

On the other hand, the moiety



has $C_{2v}$ symmetry and the two C-O bonds are equivalent, as are the two C-C bonds in the ring. This fragment has twenty-one normal vibrations ($3 \times 9 - 6 = 21$). They are grouped into four species

$$\Gamma_{red}(C_{2v}) = 8A_1 + 2A_2 + 4B_1 + 7B_2$$

Since the in-plane vibrations ($8A_1 + 7B_2$) are separable from the out-of-plane vibrations ($2A_2 + 4B_1$), all bands are infrared and Raman active.

Observation of the stretchsing and bending vibrations of the $CH_3$ groups and linked C-C stretching and C-C-C bending vibrations for all the complexes and the stretching and bending vibrations of the coordinated $H_2O$ molecules in the hydrated complexes should be observed.

The most intense bands at 1530–1560 $cm^{-1}$ are assigned to the $\nu$(C-O) and $\nu$(C-C) stretching frequencies of the complexes and are characteristic of the C-O and C-C bonds in the six-membered ring in the species of $M(O_2C_2)C\text{-}X$, which are shifted to lower frequencies compared to the corresponding single band of the free ligand which appears at 1585 $cm^{-1}$. The C-O and C-C stretching frequencies can be used to assess the covalent nature of the M-O bond. Although there is no simple relation that exists between the C-O stretching frequency and stability of the complexes, this band varies in the order.

$$\left.\begin{array}{c}\nu(\text{C-O})\\ +\\ \nu(\text{C-C})\end{array}\right\}\ \mathrm{cm}^{-1}\qquad \begin{array}{ccccccccc}\mathrm{Cr} & < & \mathrm{Cu} & < & \mathrm{Fe} & < & \mathrm{Co} & < & \mathrm{Ni}\\ 1530 & & 1540 & & 1545 & & 1550 & & 1560\end{array}$$

However, spectra in the carbonyl region are more complicated than in the lower frequency region where the M-O stretching band occurs at 440–490 $cm^{-1}$ region. It seems more reasonable to compare the M-O stretching frequencies with the stability of the complexes. The order with respect to the M-O stretching frequencies is:

$$\nu(\text{M-O})\ \mathrm{cm}^{-1}\qquad \begin{array}{ccccccccc}\mathrm{Cr} & < & \mathrm{Cu} & < & \mathrm{Fe} & < & \mathrm{Co} & < & \mathrm{Ni}\\ 480 & & 460 & & 445 & & 490 & & 440\\ & & & & & & 470 & & \end{array}$$

With the exception of the $\nu$(Co-O) of the Co(III) complexes, the latter trend resembles the one above. The discrepancy of the observed bands of $\nu$(Co-O) for the cobalt-complexes may be due to the fact that cobalt cations are bridged through OH groups which shift these bands markedly to higher frequencies as shown in Table 2.

The bands at 645–690 $cm^{-1}$ were also assigned for the $\nu$(M-O) stretching frequency and it is coupled with $\delta(C\text{-}CH_3)$ and ring deformation.

The fundamental stretching modes ν($CH_3$) for all complexes are readily assigned by comparison with the IR spectrum of the tetraacetylethane ligand which is listed in Table 2. The ν($CH_3$) stretching vibrations are assigned to broad, weak bands at 2890–2990 $cm^{-1}$ and occur at the same frequency region of the free tetraacetylethane ligand which does not show a remarkable effect on the methyl group after chelation to the metal.

The bands observed at 1000–1015 $cm^{-1}$ were assigned to $\rho_r(CH_3)$ which does not show a remarkable shift from the $\rho_r(CH_3)$ of the ligand at 1010 $cm^{-1}$. The bands observed at 930–940 $cm^{-1}$ were assigned to δ(C-C-C), which occurs at 930 $cm^{-1}$ in the free ligand. While the bands which occur at 895–915 $cm^{-1}$ were assigned to ν(C-$CH_3$) coupled with the ν(C-O) stretching frequency. The bands observed at 1310–1368 $cm^{-1}$ were assigned to the $\delta_s(CH_3)$ which does not show a significant shift from the free ligand (1310 and 1360 $cm^{-1}$). The same behaviour is repeated for $\delta_d(CH_3)$ bands observed in the range 1400–1405 $cm^{-1}$.

The bands at 1238–1260 $cm^{-1}$ were assigned as ν(C-C) + ν(C-$CH_3$) in comparison to the free ligand which shows these bands at 1245 $cm^{-1}$. The π-frequencies were observed at 500–515 $cm^{-1}$ and 405–450 $cm^{-1}$, respectively.

The IR spectra also showed very strong and broad bands at 3168–3360 $cm^{-1}$ in the Ni(II), Co(III) and Cr(III) complexes. These absorptions are assigned to the stretching vibrations of the coordinated hydroxy and/or hydroxyl groups, of water molecules or water of crystallizatioin. The related bending vibrations were assigned to the bands at 1600–1650 $cm^{-1}$ for the same complexes.

The stretching and bending vibrations of the H-bonded hydroxyl groups in the ligand are observed at 2560 and 990 $cm^{-1}$, respectively.

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