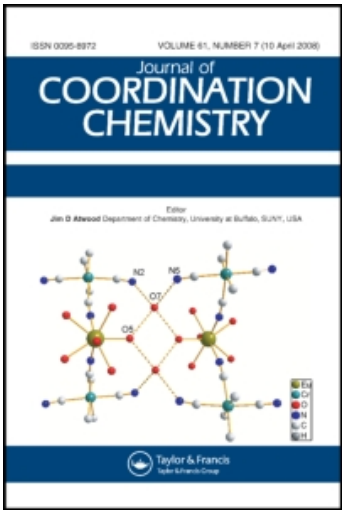

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The Preparation of Mn(II), Co(II) and Ni(II)-*bis*-3-Trifluoroacetyl-Camphorates

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To cite this Article Schurig, V.(1976) 'The Preparation of Mn(II), Co(II) and Ni(II)-*bis*-3-Trifluoroacetyl-Camphorates', Journal of Coordination Chemistry, 6: 1, 63 — 64
To link to this Article: DOI: 10.1080/00958977608079885
URL: http://dx.doi.org/10.1080/00958977608079885

J. Coord. Chem.
1976, vol. 6, pp. 63–64

SHORT COMMUNICATION
The Preparation of Mn(II), Co(II) and Ni(II)-*bis*-3-Trifluoroacetyl-Camphorates

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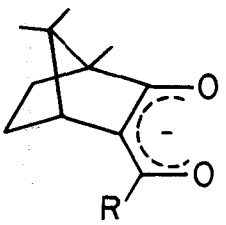
(*Received March 8, 1976; in final form June 4, 1976*)

INTRODUCTION

The 3-trifluoroacetyl-*d*-camphorate anion ($tfacCam^-$) (I) and related 3-perfluoroacyl-*d*-camphorates are versatile chiral β-diketonate type ligands for various ions.[1,2] The metal chelates are easily prepared by homogeneous exchange reactions of metal ions with barium-*bis*-3-trifluoroacetyl-*d*-camphorate[2] in non-aqueous media. Lanthanide-*tris*-tfacCam chelates have been used as chiral paramagnetic nmr shift reagents for the determination of enantiomeric compositions[3] and as selective gas chromatographic stationary phases for the reversible 1:1 association with group V and VI σ-donor substrates.[1] The ketoenolate anion $tfacCam^-$ has further been applied as stabilizing ligand in conjunction with dicarbonyl rhodium(I) for selective olefin complexation by glc[4] and as chiral co-ligand for the preparation of novel diastereo-isomeric diolefinrhodium(I) coordination compounds.[2,5] The preparation and properties of *bis*-tfacCam-chelates with divalent metal ions of the first transition row are reported here.



(I) R : CF_3
(II) R : H

EXPERIMENTAL

Preparation of the Chelates

632 mg Barium-*bis*-3-trifluoroacetyl-camphorate (1 mmole)[2] is dissolved in 20 ml acetone. 1 mmole of the metal chloride hydrate dissolved in 5 ml ethanol is added and the mixture stirred for 5 min. The white precipitate of barium chloride is filtered off and washed with acetone. The solvent of the combined filtrate is removed *in vacuo*. The residue is dissolved in 30 ml petrolether and the solution is filtered if necessary. The solution is transferred into the tube of a sublimation apparatus and the solvent is removed *in vacuo*. The residue is evacuated for 30 min at 95°C and then sublimed at 120–180°C/5.10^{-3} mm Hg. Crude yields are quantitative, however, some loss of product occurs during sublimation due to decomposition. The chelates are stable in the solid state. They are slightly hygroscopic and should be stored over P_4O_{10}. Attempts to prepare $Fe(tfacCam)_2$ failed due to aerobic oxidation yielding $Fe(tfacCam)_3$. Elemental analyses and molecular weights are listed in the tables.

According to molecular weight determinations Mn(II), Co(II) and Ni(II)-*bis*-3-trifluoroacetyl-camphorates are dimeric in n-hexane and in benzene with the exception of the Mn(II) chelate which apparently dissociates in the latter solvent. The dimeric nature and solubility of the chelates in nonpolar solvents is rather unusual for metal-β-ketoenolates.[6] Divalent metal ion β-ketoenolates are either monomeric in solution, as for Ni(II)-*bis*-dipivaloylmethanate,[7] or trimeric, as for Ni(II)-*bis*-acetylacetonate.[8] In addition, the related Mn(II), Co(II) and Ni(II)-*bis*-3-formyl-*d*-camphorates (II) are trimeric and insoluble in nonpolar solvents.[9] No dissociation of the dimeric nickel chelate in saturated hydrocarbon solvents occurs as judged from an association study of tetrahydrofuran with $[Ni(tfacCam)_2]_2$ at 100°C by glc and at 25°C by uv spectroscopy.[10] $Cu(tfacCam)_2$ and $Pd(tfacCam)_2$ are monomeric in benzene and n-hexane.

TABLE I
Analytical data of $M(tfacCam)_2$ chelates

Metal chelate	Colour	Elemental analyses %C Calcd.	%C Found	% H Calcd.	% H Found	% metal Calcd.	% metal Found
$Mn(tfacCam)_2$	yellow	52.47	52.65	5.14	5.22	10.00	9.81
$Co(tfacCam)_2$	brown	52.08	52.09	5.10	5.15	10.65	10.46
$Ni(tfacCam)_2$	green	52.11	51.37	5.10	5.29	10.61	10.58
$Cu(tfacCam)_2$	dark green	51.66	51.41	5.06	5.16	11.39	11.20

Analyses were performed by Galbraith Labs., Knoxville, Tenn., USA.

TABLE II
Molecular weight data of $M(tfacCam)_2$ chelates

Metal chelate	Molecular weight[a] Calcd.	Found benzene	Found n-hexane
$Mn(tfacCam)_2$	549.4	760	1100
$Co(tfacCam)_2$	553.5	1093	1075
$Ni(tfacCam)_2$	553.2	1116	1102
$Cu(tfacCam)_2$	558.0	567	532
$Pd(tfacCam)_2$	600.9	599	609

Analyses were performed by Galbraith Labs., Knoxville, Tenn., USA.

[a]By vapour pressure osmometry (0.01 M chelate in benzene or n-hexane).

ACKNOWLEDGEMENT

The author thanks Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for support.

REFERENCES

1. B. Feibush, M. F. Richardson, R. E. Sievers and C. S. Springer, Jr., *J. Amer. Chem. Soc.*, **94**, 6717 (1972).
2. V. Schurig, *Inorg. Chem.*, **11**, 736 (1972).
3. H. L. Goering, J. N. Eikenberry and G. S. Koermer, *J. Amer. Chem. Soc.*, **93**, 5913 (1971); V. Schurig, *Tetrahedr. Lett.*, **1972**, 3297; M. D. McCreary, D. W. Lewis, D. L. Wernick and G. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 1038 (1974); H. L. Goering, J. N. Eikenberry, G. S. Koermer and C. J. Lattimer, *J. Amer. Chem. Soc.*, **96**, 1493 (1974); J. A. Cunningham and R. E. Sievers, *J. Amer. Chem. Soc.*, **97**, 1586 (1975); V. Schurig, *Tetrahedr. Lett.*, **1976**, 1269.
4. V. Schurig and E. Gil-Av, *Chem. Commun.*, **1971**, 650; E. Gil-Av and V. Schurig, *Anal. Chem.*, **43**, 2030 (1971); V. Schurig, *Ang. Chem. Int. Ed.*, **15**, 304 (1976).
5. V. Schurig, *J. Organometall. Chem.*, **74**, 457 (1974).
6. D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).
7. F. A. Cotton and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **83**, 2818 (1961); F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966).
8. F. A. Cotton and C. M. Lukehart, *J. Coord. Chem.*, **2**, 243 (1973).
9. R. L. Lintvedt and A. M. Fatta, *Inorg. Chem.*, 7, 2489 (1968).
10. V. Schurig, R. C. Chang, A. Zlatkis and B. Feibush, *J. Chromatogr.*, **99**, 147 (1974).