

Synthesis, structure, and solution behavior of [Na · 15-crown-5][Mn(CO)₅]

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Abstract

The complex [Na · 15-crown-5][Mn(CO)₅] was synthesized by the reaction of freshly prepared Na[Mn(CO)₅] with 15-crown-5 in toluene. The formation of two liquid layers indicative of a liquid clathrate was noted immediately. The pale green, air-sensitive crystals of the complex belong to the monoclinic space group $P2_1/c$ with a 7.880(2), b 19.157(8), c 13.549(4) Å, β 101.78(2)°, and D_c 1.45 g cm⁻³ for $Z = 4$ formula units. The structure in the solid state is that of a dimer which resides on a crystallographic center of inversion. The [Mn(CO)₅]⁻ units are bridged together by sodium cations. The latter are coordinated to one equatorial carbonyl oxygen atom, one axial carbonyl oxygen atom, and the five oxygen atoms of the crown ether. The two Na...O(carbonyl) contacts are 2.409 and 2.555 Å, and the sodium ion lies 0.88 Å out of the plane of the crown ether oxygen atoms.

Introduction

Among the salts of transition metal carbonylates, there is a gradation of cation...anion interactions [1]. On the one hand there are those in which the cation exerts no significant influence upon the geometry of the anion [2], while on the other there are those in which the cation is directly bonded to the anion [3]. A very large class of the former are those in which the cation interacts with a ligand which is external to the metal coordination sphere [4]. It had been previously suggested that in the presence of a donor solvent Na⁺ interacts with [Mn(CO)₅]⁻ through two oxygen atoms of the anion [4]. Crown ethers have been used to good effect to (1) solubilize alkali metal salts in hydrocarbon solvents and (2) change the state of association of alkali metal ions with anions in solution [5*]. We report herein the interaction of 15-crown-5 with Na[Mn(CO)₅] in aromatic hydrocarbons and the novel structure of the complex in the solid state.

* Reference number with asterisk indicates a note in the list of references.

Experimental

All manipulations were carried out under a nitrogen atmosphere in an inert atmosphere glove box or by using Schlenk techniques. Benzene and toluene were dried and degassed in the normal manner. 15-Crown-5 and dimanganese decacarbonyl were purchased from Aldrich Chemical Company and used without further purification.

Synthesis of [Na · 15-crown-5][Mn(CO)₅]

A Na/Hg amalgam was prepared from Na (0.3 g) and Hg (26 g). To this was added dimanganese decacarbonyl (2.12 g, 5.3 mmol) in THF (35 ml) under nitrogen. The reaction mixture was stirred at room temperature for 30 min. The solution was removed via cannula techniques from the sodium amalgam, and the solvent was then removed under vacuo to leave a pale green powder. The powder was suspended in toluene (20 ml) and to this was added 15-crown-5 (2.35 g, 10.6 mmol) in toluene (70 ml). Two liquid layers began to form immediately. The reaction mixture was then heated overnight by which time pale green crystals in good quantity were formed. These crystals show a melting point of 90 °C (sealed capillary). The compound is very air-sensitive and turns brown on exposure to air. The product weighed 4.6 g (80% based on the manganese starting material). The reaction can be carried out in an analogous manner in benzene, *p*-xylene, and ethylbenzene. A ¹³C NMR spectrum run using a sealed NMR tube with the compound dissolved in C₆D₆

Table 1

Crystal data and summary of data collection

Compound	[Na · 15-crown-5][Mn(CO) ₅]
Mol wt	876.5
Space group	<i>P</i> 2 ₁ / <i>c</i>
Cell constants	
<i>a</i> , Å	7.880(2)
<i>b</i> , Å	19.157(8)
<i>c</i> , Å	13.549(4)
β, deg	101.78(2)
Cell vol, Å ³	2002
Molecules/unit cell	2(dimers)
ρ(calc) g cm ⁻³	1.45
μ(calc), cm ⁻¹	7.64
Radiation	MoKα
Scan width	0.80 + 0.20 tan θ
Standard reflections	200, 040, 014
Variation of standards	< 2%
2θ range	2-44
Reflections collected	2576
Reflections observed	1749
No. of parameters varied	304
GOF	0.90
<i>R</i>	0.035
<i>R</i> _w	0.038

showed a singlet at 240 ppm assigned to the carbonyl carbon atoms and one at 70 ppm due to the crown ether carbon atoms.

X-ray data collection, structure determination and refinement for [Na·15-crown-5][Mn(CO)₅]

Single crystals of the compound were sealed under N₂ in thin-walled glass capillaries. Final lattice parameters were determined from the least-squares refinement of the angular settings of 24 accurately centered reflections ($\theta > 18^\circ$) and are given in Table 1. The space group was uniquely defined as $P2_1/c$.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the $\theta/2\theta$ scan technique as previously described [6]. A summary of data collection parameters is given in Table 1. The intensities were corrected for absorption using the empirical method. Calculations were carried out with the SHELX system of computer programs [7]. The position of the manganese atom was found using standard heavy atom techniques, and subsequent difference maps revealed the positions of all the non-hydrogen atoms. The non-hydrogen atoms were refined with anisotropic thermal parameters and a subsequent difference Fourier map revealed the positions of the hydrogen atoms. The latter were given isotropic thermal parameters of 8.0 Å²

Table 2

Final fractional coordinates for [Na·15-crown-5][Mn(CO)₅]

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^a
Mn	1.05185(9)	0.18047(4)	1.01160(5)	0.037(3)
Na	0.6047(2)	0.02070(9)	0.7662(1)	0.042(4)
O(1)	0.8341(5)	-0.0447(2)	0.8932(3)	0.071(21)
O(2)	0.7700(6)	0.1079(2)	0.8727(3)	0.077(17)
O(3)	1.3954(6)	0.2069(2)	0.9625(4)	0.097(16)
O(4)	0.9255(6)	0.3158(2)	0.9175(3)	0.087(31)
O(5)	0.9862(5)	0.2324(2)	1.2057(3)	0.075(18)
O(6)	0.3358(5)	0.0694(2)	0.7842(3)	0.078(14)
O(7)	0.4321(5)	-0.0645(2)	0.8346(3)	0.075(11)
O(8)	0.5733(5)	-0.0847(2)	0.6675(3)	0.060(9)
O(9)	0.7675(5)	0.0246(2)	0.6311(3)	0.068(15)
O(10)	0.5135(6)	0.1162(2)	0.6444(3)	0.069(13)
C(1)	1.1247(6)	0.0970(3)	1.0697(4)	0.047(2)
C(2)	0.8804(7)	0.1363(3)	0.9261(4)	0.054(16)
C(3)	1.2611(8)	0.1956(3)	0.9822(4)	0.055(6)
C(4)	0.9754(7)	0.2634(3)	0.9530(4)	0.054(10)
C(5)	1.0130(6)	0.2122(3)	1.1301(4)	0.046(5)
C(6)	0.2065(9)	0.0231(9)	0.8067(7)	0.102(42)
C(7)	0.302(1)	-0.0310(6)	0.8751(7)	0.109(35)
C(8)	0.374(1)	-0.1194(4)	0.7637(6)	0.084(6)
C(9)	0.517(1)	-0.1417(3)	0.7190(6)	0.075(17)
C(10)	0.730(1)	-0.0973(4)	0.6334(6)	0.082(5)
C(11)	0.760(1)	-0.0369(5)	0.5721(6)	0.092(26)
C(12)	0.745(1)	0.0875(5)	0.5718(6)	0.098(30)
C(13)	0.668(1)	0.1432(4)	0.6253(6)	0.092(15)
C(14)	0.414(2)	0.1632(4)	0.6932(7)	0.101(49)
C(15)	0.269(1)	0.1239(5)	0.7212(7)	0.098(3)

^a $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

and were included in the refinement process. Refinement converged with $R = 0.035$ and $R_w = 0.038$. A final difference Fourier map showed no feature greater than $0.4 \text{ e}/\text{\AA}^3$. The positional parameters are given in Table 2, and the temperature factors and hydrogen atoms coordinates are available from the authors.

Results and discussion

The reaction of $\text{Na}[\text{Mn}(\text{CO})_5]$ with 15-crown-5 provided two immiscible liquid layers. The lower layer contains all of the salt and a specific amount of aromatic hydrocarbon, while the upper layer is pure aromatic hydrocarbon. This behavior of a salt in an aromatic hydrocarbon is the liquid clathrate effect [8–10], and this is the first time it has been reported for a salt of a transition metal. The A/A values [11*] for the liquid clathrates are 6.8 with benzene, 4.4 with toluene, 2.8 with ethylbenzene and 3.0 with *p*-xylene.

The structure of the title complex is shown in Fig. 1. The dimer resides on a crystallographic center of inversion with sodium ions bridging to two anions together. Each anion interacts with one sodium ion through the oxygen atom of an

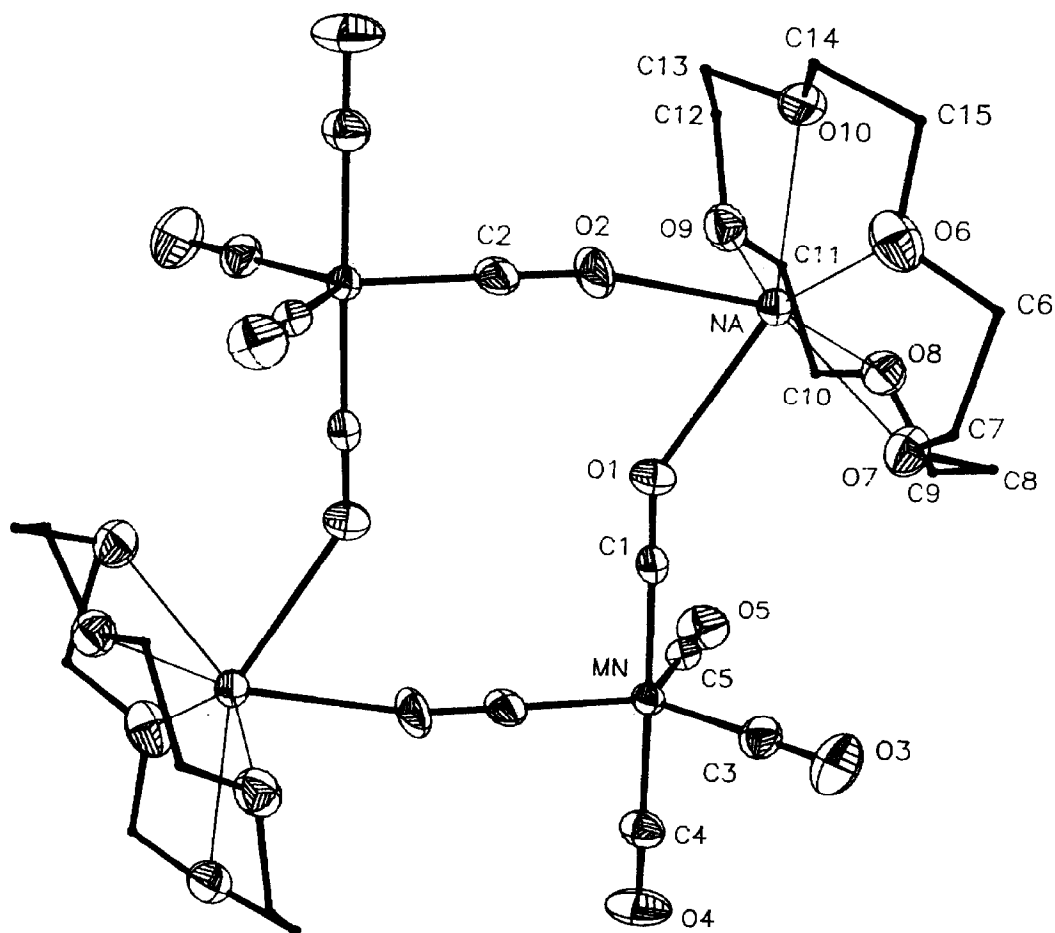


Fig. 1. Structure of the dimer of $[\text{Na}\cdot 15\text{-crown-5}][\text{Mn}(\text{CO})_5]$.

Table 3

Selected bond lengths and angles

<i>Bond lengths (Å)</i>			
Mn–C(1)	1.823(5)	Mn–C(2)	1.801(6)
Mn–C(3)	1.797(6)	Mn–C(4)	1.823(6)
Mn–C(5)	1.800(6)	Na...O(1)	2.555(4)
Na...O(2)	2.409(4)	Na...O(6)	2.373(4)
Na...O(7)	2.426(4)	Na...O(8)	2.407(4)
Na...O(9)	2.441(4)	Na...O(10)	2.471(4)
O(1)–C(1)	1.138(6)	O(2)–C(2)	1.148(6)
O(3)–C(3)	1.163(6)	O(4)–C(4)	1.146(6)
O(5)–C(5)	1.154(6)		
<i>Bond angles (°)</i>			
C(1)–Mn–C(2)	89.7(2)	C(1)–Mn–C(3)	90.9(2)
C(2)–Mn–C(3)	122.4(3)	C(1)–Mn–C(4)	179.1(2)
C(2)–Mn–C(4)	89.5(2)	C(3)–Mn–C(4)	90.0(2)
C(1)–Mn–C(5)	90.4(2)	C(2)–Mn–C(5)	119.4(2)
C(3)–Mn–C(5)	118.3(2)	C(4)–Mn–C(5)	89.6(2)
O(1)...Na...O(2)	73.4(1)	Na...O(1)–C(1)	145.9(4)
Na...O(2)–C(2)	162.4(4)	C(6)–O(6)–C(15)	113.7(7)
C(7)–O(7)–C(8)	115.8(6)	C(9)–O(8)–C(10)	114.2(5)
C(11)–O(9)–C(12)	113.2(6)	C(13)–O(10)–C(14)	115.6(7)
Mn–C(1)–O(1)	178.1(1)	Mn–C(2)–O(2)	179.0(6)
Mn–C(3)–O(3)	178.5(5)	Mn–C(4)–O(4)	178.7(5)
Mn–C(5)–O(5)	179.3(5)		

axial carbonyl group and with the other sodium ion through the oxygen atom of an equatorial carbonyl group. It is expected that the shifting of the carbonyl electron density toward the cation should increase the Mn–C bond order and decrease the C≡O bond order [1]. Indeed this has been found for 2+ and 3+ cations [12,13]. For the sodium cation in [Na·18-crown-6][W(CO)₅S] [14], the W–C(≡O...Na) length is 1.95(2) Å, compared to 2.02(1) → 2.05(1) Å for the carbon atoms of the non-bridging carbonyl groups. The error limits for the C≡O bond lengths unfortunately prevent a meaningful interpretation. It is also difficult to evaluate the effect of the K...O≡C interaction in [K·18-crown-6][Fe₄(AuPEt₃)(CO)₁₃] [15]. The Fe–C(≡O...K) length, 1.764(6) Å, is at the short end of the range of Fe–C(C≡O) lengths, 1.756(6) → 1.851(9) Å, and the C≡O distance, 1.162(7) Å, is at the long end of the range, 1.134(9) → 1.172(7) Å. However, in the title complex the interaction with the sodium ion has not significantly affected the Mn–C bond order. The two Mn–C(axial) bond lengths are identical at 1.823(5) Å, and the Mn–C(equatorial) distances range only from 1.797(6) → 1.801(6) Å. The C≡O bond order has marginally decreased upon coordination. The C≡O(axial) length is 1.138(6) Å for the coordinated carbonyl compared to 1.146(6) Å for the uncoordinated one. In the equatorial positions, the coordinated one exhibits 1.148(6) Å compared to 1.154(6) and 1.163(6) Å for the uncoordinated ones. Thus, in the solid state the interaction with the sodium ions does not significantly disturb the trigonal bipyramidal arrangement at the manganese atom.

The two Na...O(carbonyl) separations, 2.409(4) and 2.555(4) Å (Table 3), are long compared to those for formally six-coordinate sodium in [(C₅H₄CMeO)Na·

THF]_n [16], 2.295(8) and 2.329(8) Å. However, the shorter is at the low end of the range of the Na...O(crown) separations, 2.373(4) to 2.471(4) Å, and the longer is still near enough to be considered significant [17]. The Na...O(2)–C(2) angle, 162°, is near the largest such value reported, 168°, in [V(THF)₄][V(CO)₆]₂ [18]. The Na...O(1)–C(1) angle is 146°. The sodium ion lies 0.88 Å out of the plane of the crown ether oxygen atoms. This value is indicative of an attraction such as that found for the Na⁺...perchlorate in [Na·benzo-15-crown-5][ClO₄] [17], the Na⁺...picrate in [Na·benzo-15-crown-5][C₆H₂N₃O₇] [19], and the Na⁺...ethyl-acetoacetate in [Na·15-crown-5][C₆H₉O₃] [20].

Acknowledgements

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References

- 1 M.Y. Darensbourg, *Prog. Inorg. Chem.*, 33 (1985) 221.
- 2 D.J. Darensbourg, C.G. Bauch, and A.L. Rheingold, *Inorg. Chem.*, 26 (1987) 977.
- 3 J.St. Denis, W. Butler, M.D. Glick, and J.P. Oliver, *J. Am. Chem. Soc.*, 96 (1974) 5427.
- 4 C.P. Horwitz and D.F. Shriver, *Adv. Organomet. Chem.*, 23 (1984) 219.
- 5 The dimer [NaN(SiMe₃)₂]₂ is broken in aromatic hydrocarbons by the addition of 15-crown-5 or 18-crown-6: G. Lake, B. Wilhite, and J.L. Atwood, unpublished results.
- 6 J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood, and W.E. Hunter, *J. Chem. Soc., Dalton Trans.*, (1979) 46.
- 7 SHELX, a system of computer programs for X-ray structure determination by G.M. Sheldrick, 1976.
- 8 J.L. Atwood and W.R. Newberry, *J. Organomet. Chem.*, 42 (1972) C77.
- 9 J.L. Atwood in J.L. Atwood, J.E.D. Davies, and D.D. MacNicol (Eds.), *Inclusion Compounds*, Vol. 1, Academic Press, 1984, London, p. 375–405.
- 10 J.L. Atwood, S.G. Bott, A.W. Coleman, K.D. Robinson, S.B. Whetstone, and C.M. Means, *J. Am. Chem. Soc.*, 109 (1987) 8100.
- 11 The *A/A* value is the ratio of the number of aromatic molecules to anion in the liquid clathrate layer.
- 12 S.W. Ulmer, P.M. Skarstad, J.M. Burlitch, and R.E. Hughes, *J. Am. Chem. Soc.*, 95 (1975) 4465.
- 13 R.B. Petersen, J.J. Stezowski, W. Wan, J.M. Burlitch, and R.E. Hughes, *J. Am. Chem. Soc.*, 93 (1971) 3532.
- 14 M.K. Cooper, P.A. Duckworth, K. Henrick, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1981) 2357.
- 15 C.P. Horwitz, E.M. Holt, C.P. Brock, and D.F. Shriver, *J. Am. Chem. Soc.*, 107 (1985) 8136.
- 16 R.D. Rogers, J.L. Atwood, M.D. Rausch, D.W. Macomber, and W.P. Hart, *J. Organomet. Chem.*, 238 (1982) 79.
- 17 J.D. Owen, *J. Chem. Soc., Dalton Trans.*, (1980) 1066.
- 18 M. Schneider and E. Weiss, *J. Organomet. Chem.*, 121 (1976) 365.
- 19 D.L. Ward, A.I. Popov, and N.S. Poonia, *Acta Crystallogr. C*, 40 (1984) 238.
- 20 C. Cambillau, G. Bram, J. Corset, and C. Riche, *Can. J. Chem.*, 60 (1982) 2554.