Solid-state Studies. Part 11.[1] The Vibrational Spectra of Mixed Crystals of Tricarbonyl(η-mesitylene)-chromium, -molybdenum, and -tungsten in the 2 000 cm^{-1} Region

By **David N. Kariuki** and **Sidney F. A. Kettle,*** School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

Although $[Cr(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$ is not isomorphous with the corresponding molybdenum and tungsten complexes, all these complexes form an apparently continuous range of mixed crystals having the structure of the molybdenum–tungsten species. All the ν(CO) modes show one-mode behaviour. All the other modes, with the probable exception of lattice modes, show two-mode behaviour.

IN previous papers in this series we have detailed experimental data on the vibrational spectra of molecular crystals containing randomly dispersed mixtures of isomorphous metal carbonyl derivatives.[1] The components of these crystals differed in the isotopic composition of the carbonyl group, *i.e.* were mixed crystals either having a variety of x in $[MR(^{12}CO)_x(^{13}CO)_{n-x}]$, or in the nature of M. (In this latter case, one might,

---

[1] Part 10, D. N. Kariuki and S. F. A. Kettle, *Spectrochim. Acta*, in the press.

as a first approximation, also regard the different metals as isotopes rather than different elements.) The molecular symmetries of the species studied were always rather high so that those species which showed invariant two-mode behaviour indicated the order of multipolar interactions which were of importance in the intermolecular vibrational coupling which occurs in such crystals. The work reported in the present paper is the first on species in which factor-group splitting would be expected for all the modes.

Most of the theoretical and experimental work on the vibrational spectra of mixed crystals has been concerned with the low-frequency lattice-mode region.[2] The detailed band structure has therefore posed a particular problem; even with a good band model the relation with the observed spectra is not unambiguous in that hot bands and mixing of one- and multi-phonon processes are complicating factors. In our work we have reported a variety of spectral behaviour of ν(CO) vibrators in mixed-crystal systems where these complications, while present, seem to be less important. For most, but not all, modes, factor-group coupling has been observed. In contrast, the ν(MC) and δ(MCO) spectral regions in mixed crystals appear to be well described as the composition-weighted sum of the spectra of the components.

We believe that our observations on ν(CO) features may well have an applicability outside their immediate context. We cite two examples. First, it is usually found that M–Cl stretching modes show a characteristic high-frequency peak–low-frequency shoulder contour, reflecting the presence of the ^{35}Cl and ^{37}Cl isotopes. The single ν(M–Cl) peak observed in some crystalline samples could well be analogous to that which we have observed in the metal carbonyls and indicate that intermolecular vibrational coupling occurs between isotopically different vibrators with consequent loss of isotope-distinct spectral features. Secondly, in metal carbonyl preparative work it is sometimes found that the ν(CO) i.r. spectrum, often as a mull, of a product differs from that reported in the literature by an amount which is greater than can be attributed to instrumental error and which, in any case, varies from peak to peak (although the general pattern is in accord with literature data). Such phenomena could indicate the presence of impurity molecules in the crystal lattice, coupling vibrationally with the host and consequently losing their individual spectral features. As we demonstrate in the present paper, there is no requirement that host and impurity be isomorphous, although it is probable that they will have spatial similarities.

In this paper we report the vibrational spectra of tricarbonyl(η-mesitylene)metal complexes [M(C$_6$H$_3$-Me$_3$-1,3,5)(CO)$_3$] (M = Cr, Mo, or W). The local carbonyl symmetry of these complexes is C_{3v}. Thus they resemble other tricarbonyl (arene)metal species, [M(arene)(CO)$_3$], which have been extensively studied.[3-5] Although the solution spectra of the [M(arene)(CO)$_3$] species have been analysed adequately using the idealised C_{3v} symmetry of the local carbonyl environment, it has been found that interpretation of the solid-state spectra requires a factor-group approach.[3,4] The solution spectra for the three mesitylene complexes studied here have been reported earlier.[5] Buttery *et al.*[4] reported the solid-state spectra of the chromium derivative; however, no work has been published on the solid-state spectra of the molybdenum and tungsten complexes.

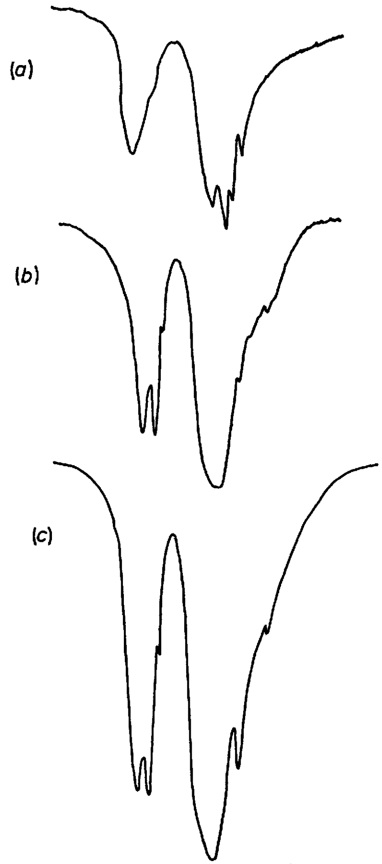

FIGURE 1 Room-temperature i.r. spectra of [M(C$_6$H$_3$Me$_3$-1,3,5)-(CO)$_3$] in the 2 000 cm^{-1} region recorded as a KBr disc. M = Cr (*a*), Mo (*b*), and W (*c*)

RESULTS AND DISCUSSION

The solid-state i.r. and Raman spectra are shown in Figures 1 and 2, and the corresponding bands are listed in Table 1. It is apparent that, while the spectra of the molybdenum and tungsten complexes are very similar, those of the chromium species are quite different. We associate this with isomorphism between the former pair but a different crystal structure for the chromium complex. Although no detailed crystal-structure analyses have been reported for these complexes,

---

[2] See, for example, H. K. Hong, *Chem. Phys. Letters*, 1973, **22**, 608; *J. Chem. Phys.*, 1975, **63**, 3687 and refs. therein.

[3] H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc.* (*A*), 1969, 2077, 2224; 1970, 471.

[4] H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc.* (*A*), 1971, 3148.

[5] R. D. Fischer, *Chem. Ber.*, 1960, **93**, 165.

preliminary data[4] indicate that the chromium species crystallises in a triclinic lattice, with four molecules per unit cell, the most probable space group being $P\bar{1}$. This implies two non-equivalent sets of molecules in the unit cell, with two molecules per set. On this basis, using a factor-group approach, six i.r. ($6A_u$)- and six Raman ($6A_g$)-active vibrations are predicted, with no coincidences occurring. As seen in Table 1 and Figures 1 and 2, the i.r. and Raman bands which are observed in the A_1 molecular region are clearly non-coincident, while the four i.r. bands in the region of the E molecularly derived mode are, to within experimental error, coincident with the four Raman bands observed in the same region. Without i.r. and Raman polarisation data it is not possible to comment on these coincidences from pure crystal studies; either i.r. or Raman data are explicable

TABLE 1

Spectra (cm^{-1}) of the complexes [M($C_6H_3Me_3$-1,3,5)$(CO)_3$]. Solution spectra were recorded in CH_2Cl_2

M = Cr			M = Mo			M = W		
I.r.		Raman	I.r.		Raman	I.r.		Raman
solution	solid	solid	solution	solid	solid	solution	solid	solid
	1 967s	1 946mw		1 959s	1 954mw		1 957s	1 950mw
1 959s	1 915(sh)	1 942mw	1 961s	1 947s	1 946mw	1 958s	1 945s	1 944mw
				1 940(sh)			1 937(sh)	
	1 882s	1 883ms		1 885b,s	1 860s		1 895(sh)	1 854s
	1 868s	1 866s			1 850w		1 880s	1 844w
1 880s			1 877s			1 875s		
	1 862m	1 861ms		1 858(sh)	1 839s		1 854m	1 833s
	1 853m	1 852s			1 833w		1 823w	1 826w
		1 833w			1 817w			1 811w
		1 821w						
		677ms			668mw			662mw
		663w			624ms			609mw
		639w			574ms			574ms
		578ms			533w			531mw
		551w			506w			506w
		516ms			491w			494w
		504mw			469mw			485(sh)
		486s			462(sh)			470s
		359mw			451s			365mw
		327s			361ms			310mw
		276mw			304ms			375mw
		198s			274ms			176ms
		121s			139(sh)			126s
		112(sh)			174ms			118s
		97s			123s			97s
		56w			115s			51mw
					96s			

TABLE 2

ν(CO) Raman bands (cm^{-1}) for mixed crystals of [$M_xM'_{1-x}$($C_6H_3Me_3$-1,3,5)$(CO)_3$] derivatives * (increments are approximately equal)

(*a*) M = Cr, M′ = Mo								
Pure [Cr($C_6H_3Me_3$-1,3,5)$(CO)_3$]	1 946ms	1 942mw	1 883ms, 1 866s	1 861ms	1 852s	1 833w	1 821w	
1 †	1 953	1 946	1 863	1 854	1 843	1 836	1 821	
2	1 953	1 946	1 853	1 853	1 843	1 836	1 820	
3	1 953	1 946	1 862	1 852	1 843	1 835	1 821	
4	1 953	1 946	1 861	1 850	1 840	1 833		1 818
5	1 953	1 946	1 861	1 850	1 840	1 832		1 816
Pure [Mo($C_6H_3Me_3$-1,3,5)$(CO)_3$]	1 954mw	1 946mw	1 860s	1 850w	1 839s	1 833w		1 817w
(*b*) M = Mo, M′ = W								
Pure [Mo($C_6H_3Me_3$-1,3,5)$(CO)_3$]	1 954mw	1 946mw	1 860s	1 850w	1 839s	1 833w		1 817w
1	1 953	1 946	1 858	1 847	1 838	1 831		1 816
2	1 953	1 945	1 858	1 848	1 837	1 831		1 815
3	1 961	1 944	1 856	1 845	1 834		1 828w	
4	1 951	1 944	1 856	1 845	1 835		1 827w	
Pure [W($C_6H_3Me_3$-1,3,5)$(CO)_3$]	1 950mw	1 944mw	1 954s	1 844w	1 833s		1 826w	
(*c*) M = Cr, M′ = W								
Pure [Cr($C_6H_3Me_3$-1,3,5)$(CO)_3$]	1 946ms	1 942mw	1 882ms, 1 866s	1 861ms	1 852s	1 831w	1 821w	
1	1 953	1 946	1 863	1 854	1 845		1 822	
2	1 953	1 944	1 861		1 841			
3	1 952	1 946	1 858		1 839			
4	1 952	1 945	1 858		1 837			
5	1 951	1 944	1 857		1 836ms			
Pure [W($C_6H_3Me_3$-1,3,5)$(CO)_3$]	1 950mw	1 944mw	1 854s	1 844w	1 833s		1 826w	

* Band intensities in the mixed crystals are similar to those of the corresponding bands in the pure components. † The numbers between the pure compounds are sample numbers of mixed crystals. The degree of enrichment in M′ increases with the sample number.

on a site-group model but, taken together, it is clear that a factor-group model is needed, at least for the region of the molecularly derived A_1 mode region.

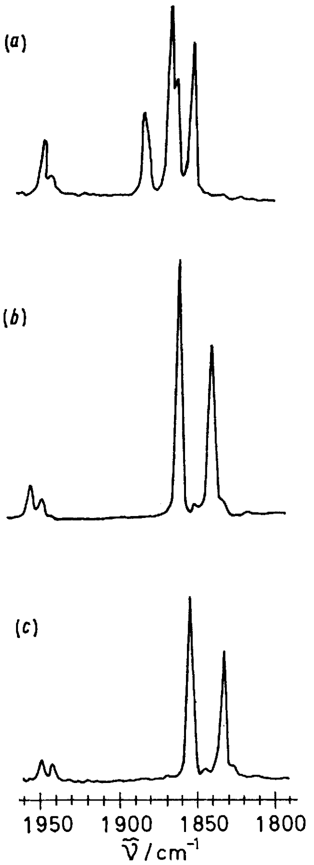

FIGURE 2 Room-temperature Raman spectra of [M($C_6H_3Me_3$-1,3,5)($CO)_3$] in the 2 000 cm^{-1} region. For details of M see Figure 1

We have not made single-crystal studies, but powder X-ray data indicate a different crystal structure for the tungsten and molybdenum complexes. These show fewer bands in their ν(CO) solid-state spectra than does the chromium analogue. Further, for each, the two i.r. bands observed in the A_1 region are nearly coincident with the two bands observed in the Raman spectra in the same region. In the E region, only two strong bands are observed in the Raman spectra. The i.r. spectra consist of one strong and broad band in the case of the molybdenum complex and of two bands, one strong, broad, and unresolved, the other of medium strength, in the case of the tungsten derivative. The i.r. and Raman bands do not show any significant coincidences.

The data from the three species are, therefore, complementary. The chromium data indicate that the molecular A_1 modes couple in the solid state whilst the data for the other two complexes demonstrate coupling between E modes. Of course, the crystal structures differ in the two cases but, unless there is a remarkable and complementary orthogonality between molecular vibrators in the two structures, the only reasonable conclusion is that intermolecular vibrational coupling occurs between all the molecular ν(CO) modes.

In Table 1 we also report low-frequency data so that ν(M–C) and δ(MCO) regions are included. In neither is there any evidence of other than site-symmetry effects.

Mixed crystals of the complexes of Cr and Mo, Cr and W, and Mo and W were prepared by co-crystallisation of the pure components from dichloromethane–hexane solutions under a carbon monoxide atmosphere followed by vacuum drying. Raman data for the ν(CO) region for all the three mixed crystal systems are given in Table 2 and Figure 3. In Table 2 the mixed crystals are arranged according to decreasing x value, as determined approximately either from the compositions of the original solutions or from the ratio of band heights in the low-frequency region of the spectra. For this purpose bands at 470 cm^{-1} for the tungsten, 451 cm^{-1} for the molybdenum, and 486 cm^{-1} for the chromium species were used. We cannot be absolutely certain that our mixed-crystal samples, either within individual crystals or one crystal compared with another, are of

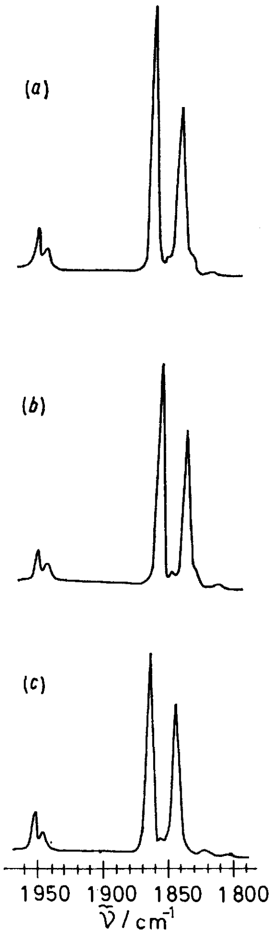

FIGURE 3 Room-temperature Raman spectra of [$M_xM'_{1-x}$-($C_6H_3Me_3$-1,3,5)($CO)_3$] in the 2 000 cm^{-1} region. The numbers on the spectra refer to the corresponding data in Table 2: (*a*) M = Cr, M′ = Mo; (*b*) M = Mo, M′ = W; (*c*) M = W, M′ = Cr

identical composition. We believe that the range of compositions present is small, first because *X*-ray powder patterns were similar to those of appropriate pure complexes and secondly because our spectra are essentially invariant with respect to a displacement of the capillary used as sample holder. The presence of inhomogeneities would presumably cause a broadening of the spectral features.

Although all the low-frequency bands in the mixed-crystal spectra show a two-mode behaviour, with frequencies equal to those in the pure components, the band of the chromium complex at 486 cm^{-1} was found to be shifted to 479 cm^{-1} in the mixed-crystal spectra. This shift is the maximum we have observed for ν(MC) and δ(MCO) vibrations in the mixed-crystal systems studied in this work.

As we have found in other cases, the bandwidths in the corresponding i.r. spectra were too great to permit the fine monitoring of behaviour which was possible from the Raman data. We therefore only report and discuss these. Although recorded at room temperature, the narrow bandwidths observed and the spectral slit width (*ca.* 1 cm^{-1}) employed enabled bands of rather different intensities 4 cm^{-1} apart to be clearly resolved {see the spectrum of [$Cr(C_6H_3Me_3$-1,3,5)$(CO)_3$]; Figure 2 and Table 1}. Frequency reproducibility was better than 1 cm^{-1} and so there is no doubt that the data of Table 2 and Figure 3, collectively, clearly demonstrate one-mode behaviour for all the ν(CO) spectral features, confirming the conclusion that all the molecular vibrations are involved in factor-group coupling.

Of particular interest is the behaviour of the chromium-containing mixed crystals. Compared to the spectra of the pure components, the spectra of the Cr–Mo and Cr–W mixed crystals show gross differences. The spectral pattern associated with the pure chromium complex disappears and the resulting spectra resemble, both in the number of bands and their intensity distribution, the spectra of the pure molybdenum and tungsten derivatives. An averaging of bands is observed in the A_1 region, the resulting frequencies approximating or even exceeding those of the component with higher frequencies. Similarly in the *E* region two of the strong bands of the chromium derivative disappear. The loss of the spectral characteristics of the chromium complex persists for very dilute mixed crystals in which it is the host lattice. It must be concluded that in the two non-isomorphous mixtures, Cr–W and Cr–Mo, the components are miscible in all proportions with, except at possibly very low concentrations, adoption of the tungsten–molybdenum lattice. This view is supported by the powder *X*-ray diffraction work. The patterns obtained from the mixed crystals of Cr and Mo or Cr and W were different from those obtained for the chromium derivative, but similar to those of the Mo–W mixed crystals and those of the molybdenum and tungsten complexes. This change in crystal structure undoubtedly also explains the shift observed in the low-frequency band of the chromium complex at 486 cm^{-1}. Although no detailed analysis was attempted, it was clear from the powder photographs that lattice parameters varied smoothly with concentration for all the mixed-crystal systems studied.

In addition to the strong Raman features discussed above, it is clear from Figures 2 and 3 and Tables 1 and 2 that there are also some very weak peaks. Further, Table 2 suggests that these exhibit either two-mode or intermediate coupling. There are several possible origins for these peaks. First, they could be factor-group modes, an explanation which could probably only be demonstrated by both a crystal-structure determination and single-crystal Raman data. However, we believe that our mixed-crystal data make such an explanation improbable. We have found cases in which a factor-group analysis was not appropriate for a particular *molecular* mode (*i.e.* in the crystal lattice such modes did not couple appreciably),[6] but it is difficult to see how factor-group effects could not occur for particular factor-group components, as required by the hypothesis under discussion. Were such a phenomenon to occur we would expect it to be in high-symmetry situations (where we have found no evidence for it) rather than the present, presumably relatively low symmetry, case. Secondly, the weak peaks could be ^{13}CO in origin. Although this may be a partial explanation (and we have found cases where it is [1,7]), we do not believe that it is a complete one. There is no reason to suppose that vibrational features associated with randomly arranged and separated ^{13}CO units should be in a 1 : 1 correspondence with those of a regularly arranged and separated lattice of ^{12}CO groups. Indeed, in some cases, where strong intermolecular vibrational coupling occurs, the effect of ^{13}CO on ^{12}CO vibrators resembles that seen in the present work of, say, ν(CO)(Mo) on ν(CO)(W): no additional features are seen, rather a shift, and possibly broadening, of a single peak.[7] A third explanation, for which we have found strong evidence in a study of salts of simple anions, is that of a lattice mode being involved in a multiphonon transition which steals intensity from a nearby allowed band.[8-10] Finally, it is possible that an overtone or combination of molecular modes is occurring, although if this were the case the frequency variability of the feature in the three cases is somewhat puzzling.

Conclusion.—The present work demonstrates two phenomena. First, that chemically similar but non-isomorphous carbonyls may co-crystallise, apparently over all the compositions, and vibrationally couple. Secondly, that in the present relatively low-symmetry case, all the factor-group components evidently display one-mode behaviour. This is important because it indicates that when, in previous studies, two-mode

---

[6] D. N. Kariuki and S. F. A. Kettle, *Inorg. Chem.*, in the press.

[7] D. N. Kariuki and S. F. A. Kettle, *Inorg. Chem.*, in the press.

[8] S. S. Ti, S. F. A. Kettle, and Ø. Ra, *Spectrochim. Acta*, 1976, **A32**, 1603.

[9] S. S. Ti, S. F. A. Kettle, and Ø. Ra, *J. Cryst. Mol. Structure*, 1976, **6**, 43.

[10] S. S. Ti and S. F. A. Kettle, *Spectrochim. Acta*, 1976, **A32**, 1765.

behaviour was observed, the explanation was to be found within the system itself (high molecular symmetry, for instance) rather than being a manifestation of some more general phenomenon.

EXPERIMENTAL

The complex $[W(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$ was purchased from Strem Chemicals Inc. and used as supplied. For the chromium and molybdenum complexes a mixture of metal hexacarbonyl (2 g) and mesitylene (15 cm^3) was heated under gentle reflux for 30 min under a slow stream of nitrogen. After cooling the mixture to room temperature, hexane (15 cm^3) was added to complete precipitation of the tricarbonyl complex. The mixture was then filtered and the solid residue washed with hexane (20 cm^3). The yellow solid was purified by recrystallisation from the minimum amount of dichloromethane under a carbon monoxide atmosphere. The resulting yellow crystals were washed with hexane (10 cm^3) and dried *in vacuo* (Found: C, 56.4; H, 4.9. Calc. for $C_{12}H_{12}CrO_3$: C, 56.3; H, 4.7. Found: C, 47.8; H, 4.1. Calc. for $C_{12}H_{12}MoO_3$: C, 48.0; H, 4.0%).

Infrared spectra were recorded as KBr discs on a Perkin-Elmer 325 spectrometer at a resolution of 1 cm^{-1} or better; Raman spectra were obtained with a Spex 1401 monochromator and Spectra Physics 165 mixed-gas laser. Incident power was generally < 10 mW.

One of us (D. N. K.) thanks the British Council for support.

[7/1337 *Received, 25th July,* 1977]