Use of Metal Isotopes in Assigning Metal–Ligand Vibrations

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Summary Use of heavy-metal isotopes provides a new and unique method to assign the metal–ligand vibrations of co-ordination compounds.

METAL–LIGAND vibrations are the most important in elucidating the co-ordination sites and the nature of metal–ligand bonds. They have been assigned by one or a combination of the following methods: (1) comparison of i.r. spectra between a free ligand and its metal complex; (2) the metal–ligand vibration should be metal-sensitive and be shifted by changing the metal or its oxidation state; (3) the metal–ligand stretching bands should appear in the same region if the metal is the same and the ligands are similar; (4) the metal–ligand vibration shows an isotopic shift if the ligand (*e.g.* $[Ni(NH_3)_6]Cl_2$–$[Ni(ND_3)_6]Cl_2$),[1] or the α-atom of the ligand (atom directly bonded to the metal) is isotopically substituted [*e.g.* oxamido(^{14}N and ^{15}N)[2] and acetylacetonato(^{16}O and ^{18}O) complexes[3]]; (5) the frequency of a metal–ligand vibration may be predictable if the metal–ligand stretching and other force constants are known *a priori*.

These methods do not, however, provide clear-cut assignments if the spectrum is complicated. We report a new method to assign the metal–ligand vibrations of complex molecules.

The use of isotopes in vibrational spectroscopy is not new.

However, no attempts have apparently been made to utilize heavy-metal isotopes to assign metal–ligand vibrations of co-ordination compounds, since (1) pure metal isotopes are not commercially available and (2) the magnitude of an isotopic shift is relatively small because of a small mass difference between metal isotopes. Recently, Oak Ridge National Laboratory has made a number of metal isotopes available for scientific research.[4] Using these, it is possible to prepare a pair of metal complexes (mg scale) in which only the metals are isotopically substituted.

The magnitude of an isotopic shift due to metal isotopes is clearly beyond the possible experimental errors in certain cases, *e.g.* the antisymmetric stretching frequencies of linear $^{58}Ni^{35}Cl_2$ and $^{60}Ni^{35}Cl_2$, in argon matrix, natural isotopic abundance, are 520·6 and 516·5 cm^{-1}, respectively.[5]

The present method of metal isotopic substitution is superior to the conventional isotopic method (4) described above, in which metal–ligand vibrations as well as ligand vibrations involving the motion of the α-atom are shifted by isotopic substitution of the α-atom.

We have prepared $^{58}Ni(PEt_3)_2Cl_2$ and $^{62}Ni(PEt_3)_2Cl_2$ (isotopic purities ^{58}Ni, 99·98% and ^{62}Ni, 99·02%) and measured their far-i.r. spectra (Hitachi-Perkin-Elmer FIS-3 i.r. spectrophotometer; Table). Previously, Goggin and Goodfellow[6] assigned one band at 402 cm^{-1} to the Ni–Cl stretching and one band at 415 cm^{-1} to the Ni–P stretching mode. The Table shows that only two bands at 403·3 and 273·4 cm^{-1} of the ^{58}Ni complex are sensitive to isotopic substitution. The band at 403·3 cm^{-1} is due to the Ni–Cl stretching mode since this band is not present in its bromo-analogue. The band at 273·4 cm^{-1} must be assigned to the Ni–P stretching since this is the only other band which is sensitive to metal isotope substitution. The band at 415 cm^{-1} reported previously may correspond to the 408 cm^{-1} band of free triethylphosphine.[7]

Far-i.r. spectra and isotopic shifts of trans-$^{58}Ni(PEt_3)_2Cl_2$ *and its* ^{62}Ni *analogue* (cm^{-1})

^{58}Ni	^{62}Ni	Shift
416·7	416·7	0·0
403·3	396·6	6·7
372·5	372·6	−0·1
329·0	329·5	−0·5
273·4	267·5	5·9
200·2	199·4	0·8
186·5	186·7	−0·2
106·8	107·5	−0·7

This work was supported by an American Chemical Society Petroleum Research Fund unrestricted research grant. Part of this work was carried out at Illinois Institute of Technology, Chicago, Illinois.

(*Received, October 2nd*, 1969; *Com.* 1494.)

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