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Synthesis and Characterization of New Class of Mixed Polysulfide Ligands of Chromium (III) Complexes

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Abstract

From the facile loss of coordinated sulfur to chromium (Cr-S) and via intermolecular insertion reaction accompanied by elimination reaction two different chromium (III) complexes; binuclear, μ-(bis L–cysteineato(S-S)disulfide) bis [(η^3) allyl - L- cysteineto (N,O,S) chromium (III)], [$Cr_2 (C_3H_5O_2NS)_2 (C_3H_6)_2 (C_6H_{10}O_4N_2S_4)$] and sodium dihydroxobis(S-methyldisulfide L-cysteinato)chromate (III) ,Na [($Cr(OH)_2$-$(C_4H_8O_2NS_3)_2$] have been synthesised and characterized by UV- visible 1R and NMR spectroscopic methods and elemental analysis techniques.

Keyword:- **Chromium (III) complex, polysulfide**

Introduction

Owing to the important biological role of chromium (III) a number of chromium (III) complexes of organosulfur, containing amino acid and mixed ligands compounds, have been prepared and shown to have Cr-S bond (1-6). This bond is labile, in contrast to inert character of Cr (d^3), and readily hydrolyses in both acid and base media (6-8). This weak linkage hydrolysis is an important process, may provide an active site, the free thiolato (R--S^-), on the otherwise a usual inert chromium (III) complex, that may give insulin mimetic glucose tolerance factor (GTF)(1). It has been shown previously that (GTF) contains Cr(III), cysteine, glycine, glutamic acid and nicotinic acid (9,10).

One of the best characterized chromium (III) complex contain two Cr-S linkages, is the solid crystal potassium (or sodium) bis-L-cysteinato chromium (III) complex, K(Cr(L-cyst)$_2$) .2H_2O(4).This complex has been used recently in our laboratory in synthesizing a novel mixed organometal –Werner chromium (III)complex of trans-bis [(trihapto)diallylmercaptocysteinato]chromium(III) hydroxide (11). So far little attention has paid to such type of organo metallic chromium in oxidation state three, and still needs more explanation have been reported for S-S formation and its bond fission (12,13), in some an easy oxidation or reduction reactions have been used, while in others the attack of nuceophilic or electrophilic reagents on S-S bond have been reported (12,13). So far, from disulfide and chromium (III) /chromium (II) mixture via redox reaction the complex thiolate(ethylenediamine) chromium (III), which contain Cr-S bond has been synthesized (5). Yet none of the other methods were found to be employed in chromium (III) complex formation. Therefore in contributsion to the previous studies of loosely Cr-S bond and its biological activies, and also to the importance of the (S-S) linkage in biological viewpoint, the current paper shows a new method in synthesizing new class of poly sulfide ligands with chromium (III) metal via insertion interaction of diallyl disulfide and dimethyl disulfide compounds into sulfur containing amino acid L-cysteine complex of Cr (III).

Experimental

All reagents used in this study were all of grades; chromium (III) nitrate, potassium hydrogen carbonate, sliver nitrate, analytical were obtained from Redial De Hanaen Seelze,Hannover,and cysteine was obtained from Fluka – Garantie. Diallyldisulfide obtained from KOCH – light laboratories LTD, England. Electronic measurements were performed on Perkin Elmer model 200 Hitachi electronic spectrophotometer. The IR spectrometerWQF-300FT, Bigijing optical instrument factory has been used for recording spectra and NMR – spectra have been recorded by the NMR spectrometer perkin Elmer R-24B60MHz ,Hitachi.

Chromium analysis was carried out following spectrophotometric method (16) and by using AA spectrophotometer WFX 120 BRAIC and C, H,N and S analysis were carried out by Iraqi exploration company in Baghdad.

Preparation of Sodium Bis (L-Cysteinato) Chromium (III) Dihydrate (I)

This complex of chromium (III) was prepared following method reported by deMeester etal (4), with slight change using $NaHCO_3$ in stead of NaOH for adjusting the pH to required values. The blue crystals were obtained and washed with ethanol and diethyl ether and subsequently analyzed as complex (I).

Preparation of μ-(Bis L–Cysteineato(S-S)Disulfide) Bis [(η3) Allyl - L- Cysteineto (N,O,S) Chromium (III)], (II)

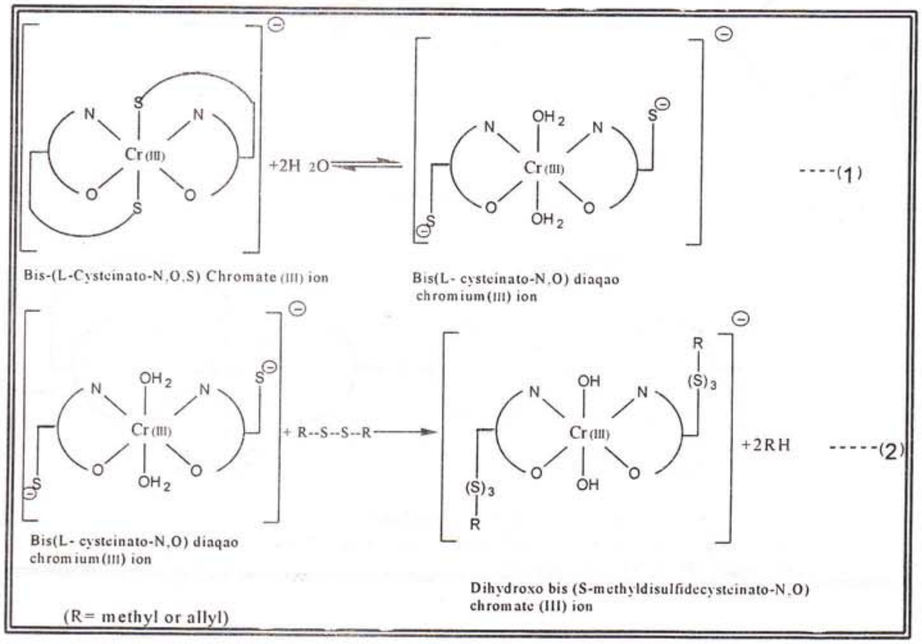
A calculated amount of compound (I) (2.8×10^{-4} mol) was dissolved in (10) ml of distilled water. Dimethyl disulfide (1.1×10^{-3} mol) was dissolved in (15) ml ethanol. The two solutions were mixed (pH 8) and refluxed for (5) hrs, until the color of mixture changes from blue to red violet. Then the mixture was allowed to cool to room temperature and left in a large evaporating dish for 24 hrs, a deep green color solid crystal was collected.

The obtained solid was washed with ethanol and diethyl ether and acetone.

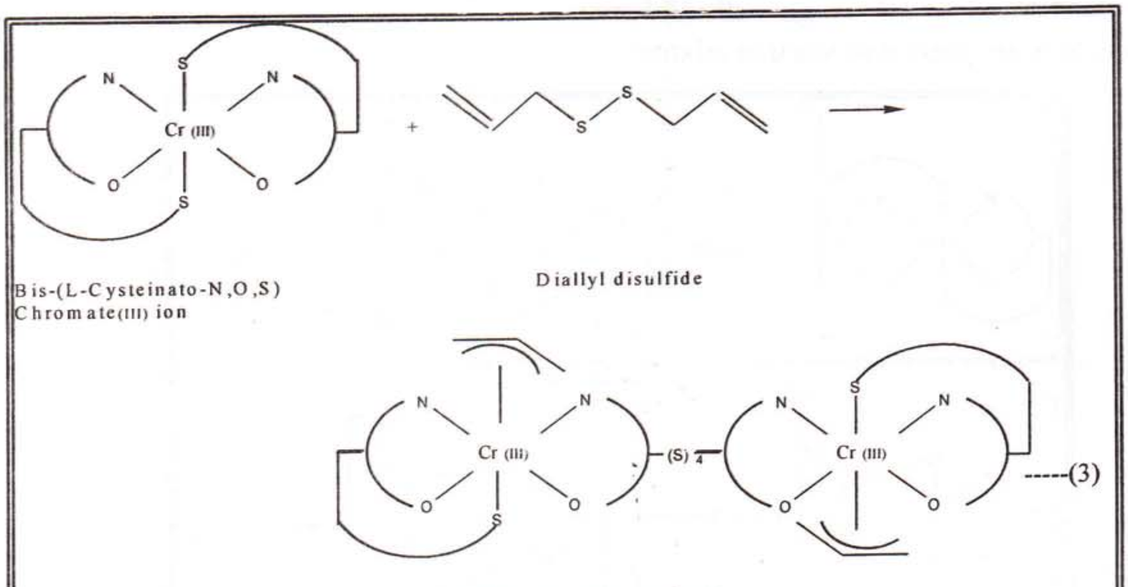
Results and Discussion

Previous investigations (6,7,8) showed that potassium or sodium salts of bis (L-cysteinato) chromium (III) complex contain a loosely (Cr-S) bond .The hydrolysis of this bond has been shown, in acid and base media, to give readily an active site thiolate ion ($R-S^-$) at physiological pHs. This leads to coordinatively unsaturated chromium (III) ion (9). However this dominant change generally promotes the activity of Cr (III) substitution reaction as well as a tendency to activate thiolato ion either to attack ,or to be attacked by other organo disulfides while they are present in reaction mixture.

In this study we observed this mode of interaction that leads to the formation of unstable tribonded at one divalent sulfur of disulfides (R-S-S-R) (d - orbitals of sulfur may faciliate this interacting) by nucleophilic attack by active thiolat ion of coordinated cysteinato (N.O) on disulfide. The intermediate results from this attack is unstable, without reduction of central chromium metal,undergoing bond fission and ultimately loses one alkyl (or allyl) fragment of organo disulfide according to the following reaction:



In reaction (1) the starting complex bis-(L-cysteinato) chromate (III) complex (I) hydrolyses and gives an active thiolato group (6,7,8) ,which prevails in reaction media and reacts with organo disulfides yielding poly -sulfide according to reaction(2). The preparative methods for tri,tetra.. poly sulfide with organic end group have been shown via electorphilic or nucleophilic attack (17).The pH increasing was observed in both cases of reaction of chromium(III) complex (I) and diallyldisulfide or dimethyldisulfide that may be due to addition of proton (H^+) to the leaving alkyl (or allyl) fragment of disulfide. This observation is in a good agreement with the result shown in equation (2). But instead of trisulfide a tetra sulfide was found in the reaction of complex (I) with diallyldisulfide .In this case if the reaction mixture containing complex (I) with diallyl disulfide in methanol solvent (water was not used due to solubility problems) the synthesized complex is neutral and insoluble in both water and organic solvents, and decompose at higher temperature $250C^0$ .The presence of Π - allyl group in this case is important because it coordinates to one vacant positions of octahedral chromium (III) .This coordination may enhance the splitting of allyl fragment from the disulfide and also its protonation ultimately gives mixed organo metallic / Werner complex of chromium (III), (II) , according to the following reaction (3).



Bis-(L-Cysteinato-N,O,S)
Chromate(III) ion

Diallyl disulfide

-----(3)

(Nutral binuclear product)
u-(bis L-cysteineato(S-S)disulfide) bis [(trihapto) allyl - L-cysteineto (N,O,S) chromium (III)

In the above reaction (3) the neutral binuclear mixed organometallic / werner chromium (III) of tetra sulfide was obtained because of the prevailing Π-allyl group,which fractionates upon coordination to chromium metal .The behavior of Π -allyl moiety has been shown recently which coordinates to chromium (III) in the synthesized bis [(trihapto)S-allylmercaptocystinato] chromium(III) hydroxide complex (11) and in some other prepared mono, di and poly (Π) organo compounds of chromium via free radical reaction (12) .

The chromium metal analysis was performed using spectroscopic procedure (16). This procedure was unsuccessful for the synthesized neutral binuclear tetrasulfide product in case of diallyl disulfide reaction .The result of analysis of other elements C,H,N were shown in table (1). According to these results, the chemical formula for the synthesized complexes have been determined as, in case of diallyl disulfide, the product is a neutral complex: $[Cr_2 (C_3 H_6)_2(C_3 H_5 O_2 N S)_2 (C_6 H_{10} O_4 N_2 S_4)]$, μ-(di L–cysteineato(S-S)disulfide) bis [(η3) allyl – L- cysteineto (N,O,S) chromium (III) complex (II), and in case of dimethyl disulfide is as sodium salt: $Na [Cr(OH)_2(C_4H_8O_2NS_3)_2]$,sodium dihydroxy bis (S-methyl disulfide L- cysteinato) chromium (III) complex (III). In these complexes, the possible ligation groups amino, carboxyl and Π -allyl have been confirmed by following spectroscopic measurements:

Table (1) Analytical Result

	% C		% H		% N		% Cr	
Compounds	**Found**	**Cacl.**	**Found**	**Cacl.**	**Found**	**Cacl.**	**Found**	**Cacl.**
$Na [Cr (C_3H_5O_2NS)_2]. 2H_2O$ (I)	20.75	20.6	4.5	4.0	8.01	8.02	1.51	14.4
$[Cr_2 (C_3H_6)_2 (C_3H_5O_2NS)_2 (C_6H_{10}O_4N_2S_4)]$ (II)	30.2	29.6	4.4	4.3	8.09	7.62	--	14.2
$Na [Cr (OH)_2 (C_4H_8O_2NS_3)_2$ (III)	19.6	19.009	3.51	3.5	4.8	5.5	11	10.29

The electronic absorption spectra of starting complexes and products were recorded in table –2. This table shows absorption bands of starting blue complex (I) in the visible region at 604nm, 540(sh),408nm ,and a band in UV region at 262nm . Upon hydrolysis of Cr-S bond and its insertion reaction with disulfides, the visible bands are blue shifted to 550nm and 405nm with disappearing UV-band at 262nm (see table –1). The band positions of each complex (II and III) were occurred in region expected to those chromium (III) complexes with two NH_2 and COO^- group donors. This result indicates that the amino and carboxyl groups remain in coordinated sphere . The IR absorption spectra were measured in the range 400-4000 cm^{-1} for the starting chromium (III) (I) and synthesed complexes (II &III) . Typical spectra for I &II are shown in Fig –1 , and the data for characteristic absorption bands are tabulated in Table –3. It is observed from this table that the band which is assign to ν (COO^-) appeared at 1660,1654 and 1646 cm^{-1} in all complexes I,II and III respectively. While the carboxyl of amino acid free cysteine in HCl was observed at 1740 cm^{-1} ,this shows red shift upon complexation. This result confirms that the carboxyl of cystein remained in chromium coordinated sphere in all complexes as mentioned a bove (14) .A broad band at ν 3200cm^{-1}, corresponding to NH2 stretching was found in all complexes, which indicates the presenced NH_2 of cystinato in coordinated sphere of all chromium (III) complexes .The more striking point is that absence of characteritic sharp band of Π - allyl ν (C=C) of diallyl disulfide in the spectrum of complex (II) upon compelxation , While the ν (C=C) of free diallyl disulfide was observed as a sharp band at 1640cm^{-1} .This band, as expected red shifted and lower appeared at 1400cm^{-1} (14,15). On complexation Π -allyl with chromium center , the υ (C=C) coalesced with sym ν C=O stretching band of cystein in IR-spectrum. This result quite well agree with the suggested Π -allyl group coordinated in organochromium (III) complexes (II) through Π and this is more confirmed by resonance proton spectrum results.

Table (2) Visible- Electronic Spectra

		Visible		
Compounds	**Color**	**λ 1 (nm)**	**λ 2 (nm)**	**λ 3 (nm)**
Na [Cr ($C_3H_5O_2NS)_2$]. $2H_2O$ (I)	Blue	604	540 (sh)	408
[Cr_2 ($C_3H_6)_2$ ($C_3H_5O_2NS)_2$ ($C_6H_{10}O_4N_2S_4$)] (II)	Brown	540*		400*
Na [Cr $(OH)_2$ ($C_4H_8O_2NS_3$) $_2$ (III)	Deep green	556		405

* desolved in DMSO

Table (3) Characteristic Absorption Bands in the IR Spectra of the Synthesized Chromium (III) Complexes and Starting Compounds

Diallyl disulfide cm^{-1}		**Dimethyl disulfide cm^{-1}**		**Compound (I) cm^{-1}**		**Compound (II) cm^{-1}**		**Compound (III) cm^{-1}**	
ν S − S	510 m	ν S-S	506 w	ν Cr − N	478 w	ν Cr − N	478 w	Cr − N	480 w
ν C − S	690 m	ν C-S	620 w	ν Cr − O	542 w	ν Cr - O	515 w	Cr − O	542 w
ν CH_2	950 s	ν_s CH_3	1375 m	ν Cr − S	690 w	ν Cr − S	555 w	Cr − S	Notvisible
ν C − H	2930 s	$\nu_{as}$$CH_3$	1450 s	ν C-S	670 w	ν S - S	675 w	COO $_{sy}$	1384 s
ν C = C	1640 s	ν_S C − H	2872 s	ν C-O	1260 m	ν_s COO	1402	COO $_{asy}$	1646
ν =C− H	3078 s	ν_{as} C − H	2962 s	ν_s COO	1400 s	δ NH_2	1560 m	ν C −H_{st}	2943
				δ NH_2	1560 m	ν_{as} CO O	1654 s	ν NH_2	3200
				ν_{as} C O O	1660 s			O − H	3430 b
				ν C − H	2956 w				

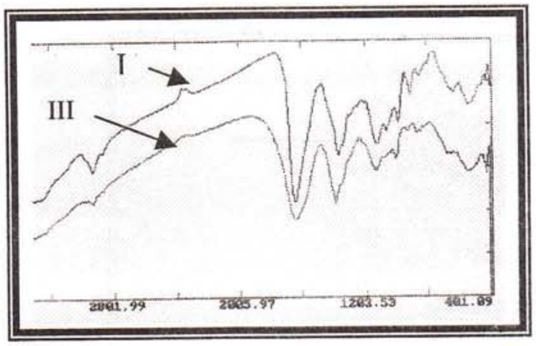


Fig – 1 – The IR spectra of; binuclar μ-(di L–cysteineato(S-S)disulfide) bis [(η3) allyl – L- cysteineto (N,O,S) chromium (III)complex (II)and sodium dihydroxo bis(S-methyl disulfide L- cysteinato) chromium(III) of complex (III) .

The NMR spectra for both synthesized complexes (II) & (III) were taken and shown in fig -2-. This figure shows that the proton signals are all strongly shieled by chromium (d^3) metal, therefore they are appeared as a coalescing band in both spectra in the range (2- 4.5δ). While within the mentioned range, a doublet signal of nearly the same intensity was observed at (3.3δ) in the spectrum complex (III), this is assigned to terminal methyl group. The resonances of protons of the free allyl group of diallyl disulfide were observed in the range (4.5 –6 δ). These signals are completely shielded and shifted to high field and all appeared as a group broad band at (2.7δ). These observed NMR results, the IR data and other physical measures support that the allyl group linked to chromium center as trihapto and leaves a terminal methyl group free. This Π -doner site can gives a high electron density to the metal probably stabilize (or assist recoordinating) the trans coordinated Cr-S bond of cysteinato at pH8, because both σ and d - orbitals of sulfur atom decrease the electron density on the central metal of the synthesized compound (II).

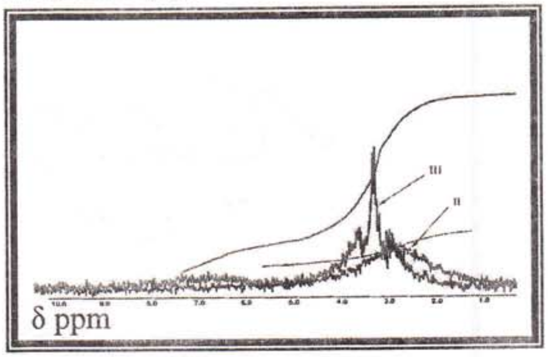
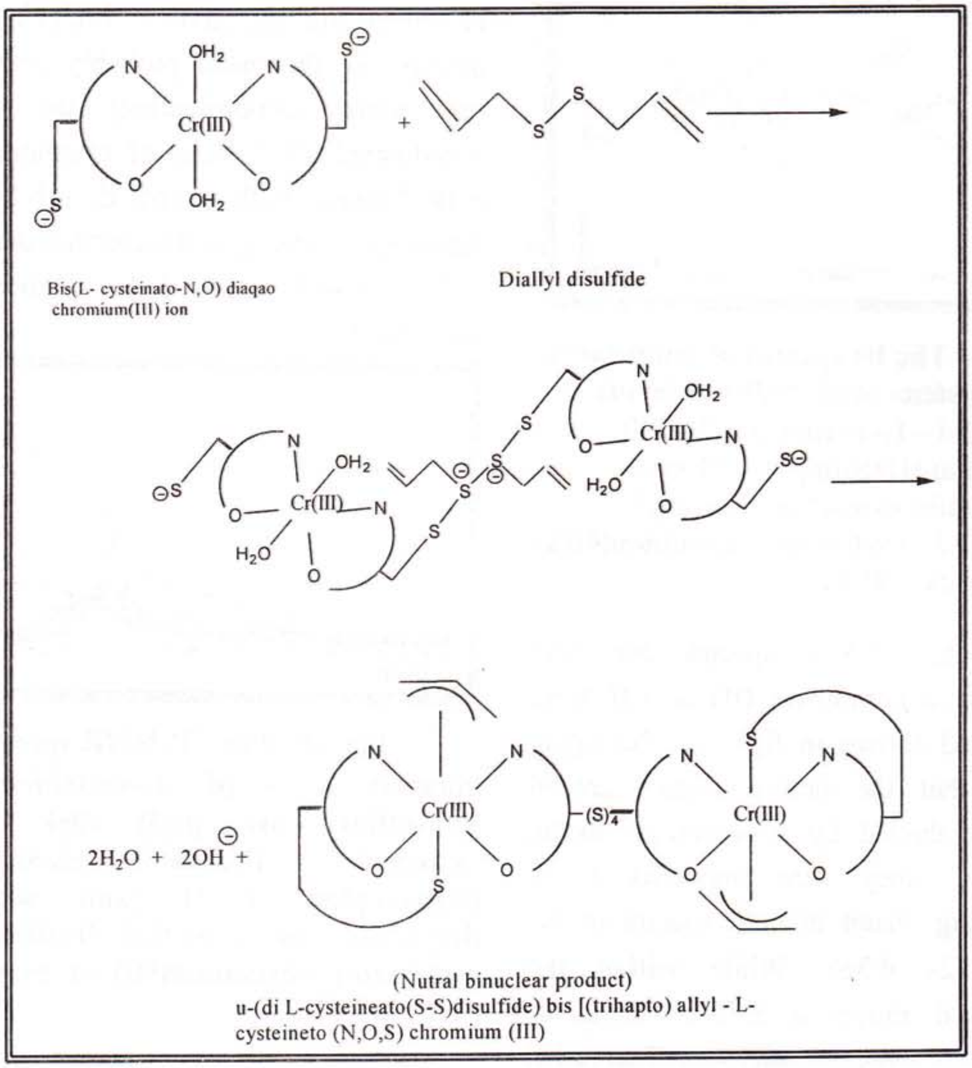


Fig -2- The ¹H NMR spectra of binuclar μ - (di L–cysteineato(S-S)disulfide) bis [(η3) allyl - L-cysteineto (N,O,S) chromium (III)complex (II)and sodium dihydroxo bis(S-methyl disulfide L-cysteinato) chromium(III) of complex (III) in DMSO.

So under our experimental conditions using solvent ethanol (or methanol) and at pH 7-8 it is possible the allyl group coordinate to chromium (III) center after the C - S bond cleavage of the organo disulfide intermediate. This clevage following the protonation at the terminal allyl group forming new mixed organo werner tetra sulfid complex II according to following scheme:



Conclusion

The reaction of chromium (III) complex of organo sulfur amino acid ligand ,which has loosely or unacceptable Cr-S bond ,with organo disulfide in organic (or organic/water) solvent leads to formation new of class of coordinated poly sulfide complexes (in near physiological pHs) .Therefore, the synthesized method described in the current study can be used as a new rote to synthesize tri,tetra (or may be poly) organosulfide without involving oxidation reduction at the central metal.

The reported results also suggest use. This new rote in synthesizing mixed organometallic /Werner complexes of chromium (III). Which up to date none of these organo metal complexes of Cr (III) have been synthesized.

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ئامادەکردن و ناسینەوەی هەندێ ئاڵۆزی نوێی کرۆم (III) لەگەڵ لیگاندی پۆلی گۆگردیدا

ئامادەکردن و ناسینەوەی هەندێ ئاڵۆزی نوێی کرۆم (III) لەگەڵ ایگاندی پۆلی گۆگردیدا

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پوختە

دوو ئاڵۆزی نوێی کرۆم (III) کە لیگاندی سیانەو و چوارە سلفایدی تێدایە بە ڕێگەی سوود وەرگرتن لە هەڵوەشاندنەوەی ئاوی بوندی (Cr –S) ی لاواز وە کارلێکی چونە ناوەوەی بەندبوون وە جیابوونەوەی کیمیای ئامادەکران بە ڕێگەکانی شەبەنگی تیشکەکان بینراو و سەرو وەنەوشەیی و ژێر سوور و لەرینەوەی موگناتیسی ناوکی و ڕێگەی شیکردنەوەی ووردی توخمەکان ناسراوەتەو و دیاری کراون.

تحضير و تشخيص بعض معقدات الكروم (III) الجديدة مع خليط لكندات عضوية متعددة سولفايد

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الخلاصة

تم تحضير مركبين جديدين لمعقد كروم (III) الحاويتين على علة ليكاندات ثلاثية او رباعية لسلفايد من تفاعل مباشر للتحلل المائي لأصرة (Cr – S) الضعيفة مع المركبات سلفايدات الثنائية العضوية بطريقة تفاعل الادخال والربط الكيميائي، وثم تم تشخيص الناتج باستخدام طرف الطيفية لأشعة الاليكترونية المرئية والفوق البنفسجية وأشعة تحت الحمراء وطيف الرنين النووي والمغناطيسي وكذلك استخدام التحلل الدقيق للعناصر.

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